Department of Chemical Engineering

Properties of Bio-oil-Based Fuel Mixtures: Biochar/Bio-oil Slurry Fuels and Glycerol/Bio-oil Fuel Blends

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

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Signature: ……

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To my beloved family

ABSTRACT

Global utilization of fossil fuel is known to increase green-house gases emissions, which consequently contribute to global warming and other environmental problems. Biomass is of increasing importance in sustainable energy supply as it can be of low cost and small carbon footprint. However, the bulky and fibrous nature of biomass requires the fuel to be further pre-treated or converted into high energy density biofuels such as biochar and bio-oil. At the same time, biodiesel is considered to be an important renewable transport fuel. However, sustainable development of biodiesel industry has been impeded by the generation of a huge surplus of by-product (glycerol). While extensive research efforts have been made in utilization of glycerol for energy application, there is still considerable scope for developing new and innovative strategies for co-utilisation of biochar, bio-oil and/or glycerol.

This PhD thesis reports the fuel properties of two bio-oil-based fuel mixtures, i.e. biochar/bio-oil slurry fuel (hereafter referred to as "bioslurry") and glycerol/bio-oil fuel blends. The specific objectives are to (1) establish a suitable quantification method for analysing alkali and alkaline earth metallic (AAEM) species in bio-oil and bioslurry fuels; (2) evaluate the evolution of fuel properties during bioslurry ageing and apply the newly-developed method to quantify the distribution of AAEM species between biochar and bio-oil phase during bioslurry storage; (3) understand the mechanisms governing the leaching of nutrients in biochar by bio-oil in a bioslurry system; (4) examine the solubility of glycerol in bio-oil and characterize the fuel properties of the obtained blends; and (5) assess the possibility of blending crude glycerol into bio-oil and provide feasible strategy for integration of such blending process into biodiesel production process. These objectives have been successfully achieved and the main outcomes are summarized as follows.

Firstly, a new method has been developed and established for the quantification of AAEM species in bioslurry fuels. The so-called *evaporation-ashing-digestion-IC* method consists of four steps including evaporation that converts bioslurry into solid-like residue, ashing that converts the residue into ash, acid digestion that dissolves the ash into a solution and ion-chromatograph (IC) analysis that quantifies the AAEM species in the solution. The novelty of the method is the combination of the evaporation step with the existing ashing−digestion−IC method that is developed for solid fuels but not suitable for bioslurry fuels. The conventional ashing–digestion–IC method underestimates the concentration of AAEM species in bioslurry fuels due to carry-over of biochar particles during ashing. The evaporation step consists of multi-steps of slow heating and holding at various segment temperatures corresponding to the boiling points of the major compounds in bio-oil, resulting in progressive evaporation of bio-oil vapours with little carry-over of biochar particles. The new method has been successfully applied to quantifying AAEM species in bioslurry fuels with various biochar loading levels (5–20 wt%), with small relative standard errors (within ±3%) and low limitations of quantification (0.4−3.0 ppm). It also overcomes the biochar incomplete oxidation issue associated with the microwave-digestion-based methods, which has been found to considerably underestimate the concentrations of AAEM species in bioslurry fuels.

Secondly, ageing of a series of bioslurry fuels with different biochar loading levels was carried out at room temperature for a storage period of 29 days. The results demonstrate that the storage of bioslurry results in a reduction in the acidity (total acid number i.e. TAN), a reduction in the viscosity and an increase in the water content of the bio-oil phase. Compared to the blank bio-oil samples, the presence of biochar leads to more severe changes in the fuel properties of bioslurry, at least partially due to some condensation reactions among bio-oil compounds catalysed by the biochar or reactions between the acidic bio-oil and the basic biochar. An increase in biochar

loading level further decreases the TAN and viscosity of bio-oil phases and increases the water content of bio-oil phases. However, after 29 days of storage, the bioslurry fuels (with up to 15% biochar loading) are still acidic. In addition, the storage of bioslurry also results in undesired redistribution of AAEM species between the biochar and bio-oil phase in bioslurry, via the leaching of these inorganic species from the biochar into the acidic bio-oil by two-step kinetics.

Thirdly, the migration of AAEM species in bioslurry was further investigated via leaching of biochar by bio-oil model compounds. It is found that acids and water in bio-oil water soluble fraction is responsible for the majority of AAEM species leached from biochar by bio-oil. Other individual organic compounds in bio-oil (e.g., methanol, acetone and guaiacol) have poor polarity or low dielectric constant so that the capability for leaching of AAEM species seems to be limited. However, the presence of these organic compounds can have significant impact on the leaching capability of water or acids. For example, the presence of organic compounds with low polarity or low dielectric constant can hinder the leaching of AAEM species by water, which can be attributed to the decrease of salt solubility. On the other hand, in the presence of phenolic compounds, the leaching of AAEM species (especially Mg and Ca species) may be enhanced because these phenolic compounds improve the accessibility of AAEM species within the biochar structure by water or acid.

Fourthly, even though no measurable amount of glycerol is found soluble in bio-oil, homogenous fuel blends can be prepared with appropriate amount of methanol addition. Compared to the bio-oil or glycerol alone as a fuel, the obtained glycerol/methanol/bio-oil blends have improved fuel properties (higher heating value, lower viscosity and lower surface tension etc.). Taking safety into consideration during storage and transportation of a fuel and the possible ratio of glycerol to methanol that may be obtained from biodiesel production process, potential feasible compositions of

the glycerol/methanol/bio-oil blends (glycerol ≤ 20 wt %, methanol ≤ 10 wt %, bio-oil ≥ 70 wt %) are recommended as burner fuel for combustion applications. Further accelerated aging experiments of selected fuel blends in the recommended composition range indicate that the fuel blends experience decreases in the viscosity and TAN, and an increase in water content upon long term storage.

Fifthly, further efforts were made to investigate the possibility of directly blending crude glycerol with bio-oil, via studying the effect of major impurities in crude glycerol on solubility and properties of glycerol/methanol/bio-oil blends. The major impurities in crude glycerol considered in this study include water, soap, NaCl and NaOH. All these impurities are found to worsen the solubility of glycerol in bio-oil to some degree. In general, NaCl and NaOH can worsen the solubility even at a low concentration of 2% in glycerol because of their capability to aid phase separation of bio-oil. The effects of water and soap on solubility become significant when the ratios of water to bio-oil or soap to bio-oil are over 0.3 and 0.01, respectively. Although the impurity-containing glycerol/methanol/bio-oil blends show similar rheological properties and fuel properties (heating value, surface tension and density etc.) as to that of the glycerol/methanol/bio-oil blend, a slight reduction in acidity of the fuel blends is observed while there is a high content (e.g., 10%) of NaOH in the aqueous glycerol mixture. Ageing studies on the composed fuel blends suggest that soap or NaOH as alkaline matter can slightly slow down the changes in the fuel properties (viscosity, water content and TAN) during long term storage, especially changes in TAN. Efforts were also made to investigate the solubility of the formulated crude glycerol (FCG) in the bio-oil and fuel properties of the FCG/methanol/bio-oil blends. The results suggest that the biodiesel production process without water addition, which is used to aid phase separation and neutralisation of glycerol phase, is a good option for integration with the blending process of crude glycerol and the bio-oil to make fuel blends.

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LIST OF PUBLICATIONS

Papers Published in Refereed International Journals

[1] **Mingming Zhang** and Hongwei Wu. Effect of Major Impurities in Crude Glycerol on Solubility and Properties of Glycerol/Methanol/Bio-oil Blends, *Fuel* **2015**, 159, 118–127.

[2] **Mingming Zhang** and Hongwei Wu. Bioslurry as a Fuel. 6. Leaching Characteristics of Alkali and Alkaline Earth Metallic Species from Biochar by Bio-oil Model Compounds. *Energy & Fuels* **2015**, 29, 2535−2541.

[3] **Mingming Zhang** and Hongwei Wu. Phase Behavior and Fuel Properties of Bio-Oil/Glycerol/Methanol Blends, *Energy & Fuels* **2014**, 28, 4650-4656.

[4] **Mingming Zhang,** Suiboon Liaw, and Hongwei Wu. Bioslurry as a Fuel. 5. Fuel Properties Evolution and Aging during Bioslurry Storage, *Energy & Fuels* **2013**, 27, 7560-7568.

[5] **Mingming Zhang,** Xiangpeng Gao, and Hongwei Wu. A Method for the Quantification of Alkali and Alkaline Earth Metallic Species in Bioslurry Fuels, *Energy & Fuels* **2013**, 27, 6823-6830.

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CHAPTER 1 INTRODUCTION

1.1 Background and Motive

As the primary energy source worldwide, fossil fuels are finite and the use of such fuels can significantly contribute to global warming and other environmental issues due to various emissions including carbon dioxide, sulphur dioxide and other pollutants.[1] Therefore, alternative energy sources are of critical importance to future sustainable development. Biomass, which can be a renewable and carbon neutral source depending on its production process, has attracted increasingly attention and is recognized as an important candidate for substituting fossil fuels to address the related adverse environmental issues.[2] However, the application of biomass has been limited due to several undesired fuel characteristics of biomass (e.g., bulky nature and poor grindability).

Biomass pyrolysis, particularly biomass fast pyrolysis, is widely accepted to be an important technology for converting the bulky and poor grindable biomass into high volumetric energy density bio-oil and biochar products.[3-6] Substantial research and development have been carried out on comprehensive characterization and application of bio-oil.[7-19] As a fuel, bio-oil suffers from undesirable properties such as high water content, high acidity and poor stability.[20-22] Bio-oil may be upgraded and/or refined to produce liquid transport fuels, potentially taking advantage of the vast existing infrastructure for conventional petroleum refinery.[7-16] There are various pathways for bio-oil upgrading.[7-16] One near term application is production of bioslurry via suspending fine biochar particles in bio-oil, which was initially attempted by commercial developers (e.g., Karlsruhe[23]). Such a concept not only enhances the energy density of bio-oil, but also addresses the issues related to fine biochar particle transportation and storage.[24]

Bioslurry fuels were investigated in previous studies, including understanding the rheological properties and other fuel properties (e.g., viscosity, surface tension and static stability) of bioslurry freshly prepared from biochar and bio-oil/bio-oil fraction.[25-28] However, there is still considerable scope for research into bioslurry fuels. For example, it is known that bio-oil is prone to ageing during storage and such ageing process may be accelerated by inherent catalysts (particularly alkali and alkaline earth metallic (AAEM) species).[29-35] It would be of great importance to investigate the long term stability or ageing of bioslurry fuels. In addition, there is also a lack of fundamental understanding on the distribution of AAEM species in bioslurry fuels. This is essential to bioslurry applications, considering the significant role of AAEM species in thermochemical processing of various fuels,[36-38] high retentions of AAEM species in bioslurry,[35,39]and acidic nature of bio-oil.[18,22] Yet, thus far, little has been done on these important respects.

Biodiesel is another promising alternative fuel to substitute petroleum diesel.[40-42] The global production of biodiesel has been growing rapidly in recently years due to the easy adaptability of biodiesel in diesel engine and government supports.[43,44] The rapid growth of biodiesel industry has resulted in a huge stockpile of glycerol as by-product.[43,45] Proper utilization of such a by-product is of great importance because disposal of glycerol as waste is neither economic nor environmentally friendly.[45-47] Crude glycerol from biodiesel production process usually contains various impurities and therefore is of low market value.[48-50] Purification is an expensive process and lack of capability to accommodate large quantity of crude glycerol.[43] Alternatively, combustion or gasification can be promising pathways for glycerol or crude glycerol utilization for energy production. However, high viscosity of glycerol and high content of certain impurities may cause some difficulties in combustion/gasification application of glycerol.[51,52] One possible solution to mitigate the problems associated with glycerol alone as a fuel is to mix glycerol with other

fuels. Even though mixing glycerol with yellow grease or fuel oil has been attempted, difficulties in maintaining homogeneous fuel blends due to the large immiscibility of glycerol and grease/fuel oils have limited the application of the obtained fuel blends.[47,53] Therefore, there is a great need to develop fuel blends with alternative fuels. Bio-oil containing both polar and nonpolar compounds[54] seems to be a prospective candidate for blending with glycerol. Such application may be integrated into biodiesel production process to enhance the value chain, if impurities in crude glycerol can be tolerated in the blending process. However, there is little information on the solubility of glycerol in bio-oil and the influence of impurities in crude glycerol on the solubility of such a system.

1.2 Scope and Objectives

The present study aims to fundamentally investigate properties of two bio-oil-based fuel mixtures. The detailed objectives of this study are:

(1) To develop a method for quantification of AAEM species in bio-oil and bioslurry fuels;
(2) To evaluate the changes in fuel properties and the distribution of AAEM species in the bio-oil and biochar phases during bioslurry storage;
(3) To understand the leaching characteristics of biochar by bio-oil model compounds and water soluble fraction of bio-oil;
(4) To produce and characterize fuel blends from bio-oil and glycerol;
(5) To access the feasibility of blending bio-oil with crude glycerol via fundamental research into the effect of impurities in crude glycerol on the solubility and fuel properties of glycerol/bio-oil blends.

1.3 Thesis Outline

There are a total of 9 chapters in this thesis (including this chapter) as listed below. The thesis structure is schematically shown in the thesis map (see Figure 1-1).

- Chapter 1 introduces the background and objectives of the current research;
- Chapter 2 reviews the up-to-date literatures on the significance of thermochemical conversion of biomass, properties and applications of bio-oil, utilization of biochar and glycerol and recent advancement in bio-oil-based fuel mixtures, finally leading to the identification of existing research gaps and specific objectives of the present study;
- Chapter 3 summarizes the research methodology and techniques employed to achieve the research objectives, together with detailed explanations of the experimental equipment, analytical instruments and samples used;
- Chapter 4 examines three different methods for determining the contents of AAEM species in biochar, bio-oil and bioslurry fuels, and further develops a suitable method for quantifying AAEM species in bio-oil and bioslurry;
- Chapter 5 investigates the evolution in fuel properties and the ageing of bioslurry fuels during storage;
- Chapter 6 reports a fundamental investigation into the distribution of AAEM species in a bioslurry system via the leaching of biochar using bio-oil model compounds;
- Chapter 7 accesses the possibility of blending glycerol into bio-oil with the aid of methanol and characterizes the fuel properties of the obtained fuel blends;
- Chapter 8 demonstrates the influence of major impurities in crude glycerol on the solubility and properties of glycerol/methanol/bio-oil fuel blends;
- Chapter 9 draws the major conclusions from the present study and also lists the recommended future work.

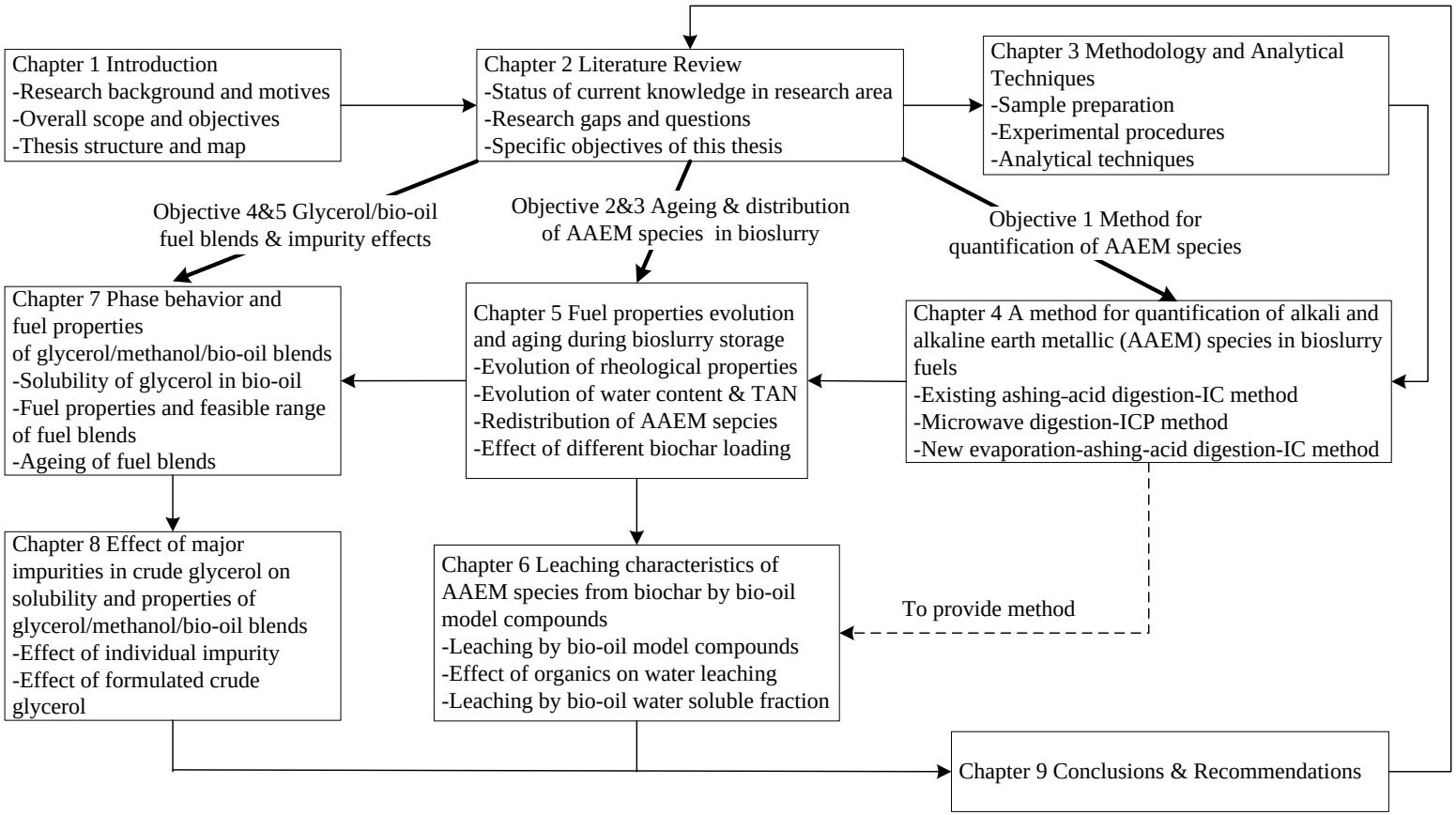

Figure 1-1 Thesis map

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The past two decades witnessed substantial research efforts dedicated to the development of clean and sustainable energy and fuel technologies.[2,55] Biofuels derived from renewable biomass have attracted extensive research interests.[56,57,60,61] Bio-oil from biomass pyrolysis and biodiesel from transesterification of vegetable oil or fat are recognized as prospective liquids to replace part of petroleum-derived fuels.[40-42,58,59] Utilization of the by-products (i.e. biochar or crude glycerol) is important to sustainable development of bio-oil and biodiesel industry, particularly of the latter.[45-47,60]

There have been extensive studies on biodiesel (including production and utilisation),[61-63] and bio-oil from biomass pyrolysis (including production, property characterization, application and upgrading techniques).[18,21,64] Meanwhile, investigations were also carried out on various pathways for utilization of the by-products (biochar and glycerol).[43,51,65] The objective of this chapter is to review the properties and utilization of bio-oil, biochar and glycerol. The review starts with the importance of thermochemical conversion of biomass, especially fast pyrolysis technology, and then moves to the chemical/physical characterization and catalytic upgrading of bio-oil for fuel application, followed by discussion on challenges in utilization of biochar and glycerol. A brief summary is also given on the recent advancement in bio-oil-based fuel mixtures. This chapter concludes with the identified research gaps and the scope of this PhD thesis.

2.2 Thermochemical Conversion of Biomass

2.2.1 Biomass as a Fuel

Fossil fuels are finite and the use of these fuels leads to adverse environmental impacts. Therefore, biomass has become an important alternative energy source. Biomass refers to all organic materials that stem from plants (including woody plants, herbaceous plants/grasses and aquatic plants) and animal, human and industrial wastes.[66,67] Consumption of biomass as a fuel source has been growing rapidly worldwide.[55] For example, in European Union, the average growth rate of biomass usage is about 2.5% per year over the last decade.[2] By 2050, the demand for biomass source is expected to increase three-fold of the current biomass demand.[68]

Traditional utilisation of biomass is for heat application, and energy production from such application of biomass accounted for 18% of total global energy used for heating in 2011.[69] As a fuel, biomass has its advantages in being renewable, potentially carbon neutral and relatively cheap.[67] However, practical application of biomass is limited by some of its undesirable properties. For instance, biomass has lower heating value than conventional fossil fuels due to its high moisture content and particular chemical composition (i.e. low carbon and high oxygen).[55,66] The bulky and fibrous nature gives biomass a poor grindability, thereby adversely affecting plant milling cost, feeding process and handling operations.[70] The poor grindability of biomass also results in production of large biomass particles with low bulk and volumetric energy density, thereby increasing transportation and storage costs.[71] Biomass fuel is also heterogeneous so that knowledge on individual biomass component is required for handling the fuel mixture with flexibility.

Biomass may be thermochemically or biochemically converted to other densified fuels that may mitigate the undesired features associated with biomass as a direct fuel.[72] In comparison to biochemical process, thermochemical conversion of biomass is

considered to have broader prospects due to its shorter reaction time and stronger capability to break down organic structures of biomass.[55,73,74]

2.2.2 Thermochemical Conversion Technologies

Thermochemical conversion processes mainly include pyrolysis, combustion, gasification and liquefaction.[72,75] As shown in Figure 2-1, combustion application generally aims at heat generation, while gasification (a partial combustion process) of biomass produces valuable fuel gases that can then be used in turbines or transport fuel synthesis.[55,75,76] Liquid products can be obtained from both pyrolysis and liquefaction of biomass. However, process conditions of these two techniques differ significantly in terms of temperature, pressure, feedstock requirements and catalysts.[58] Comparatively, pyrolysis technology is more promising due to low capital and operating costs.[58] Pyrolysis can be categorised into slow pyrolysis, which is commonly used for production of charcoal or biochar, and fast pyrolysis that primarily targets for liquid product (bio-oil).[55,77,78] Recent research on biomass pyrolysis has led to some interesting developments.[79-85]

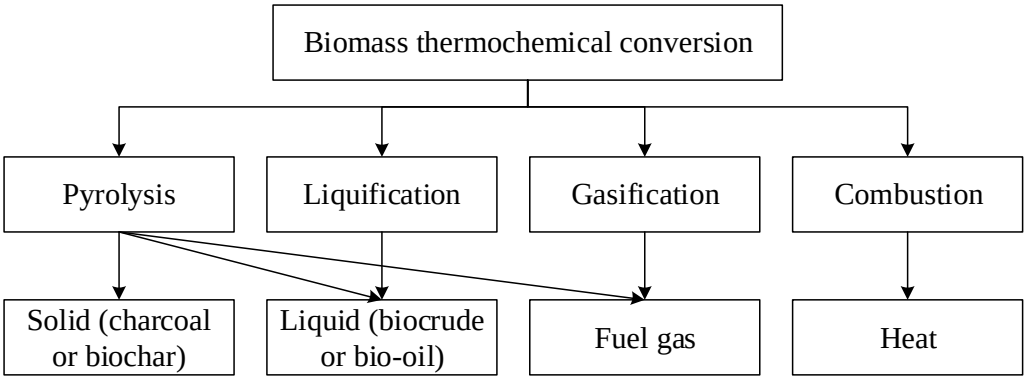

Figure 2-1 Thermochemical conversion of biomass and corresponding products[75]

2.2.3 Fast Pyrolysis

Fast pyrolysis is a promising technology that converts bulky biomass into

high-energy-density bio-oil and biochar products.[3-6] The key features of fast pyrolysis are summarized as follows:

- **High heating and heat transfer rate** at the biomass particle reaction interface.[64] This can be achieved by optimizing reactor configuration or using small biomass particles. Typical fast pyrolysis reactors include fluidised bed reactor, ablative reactor, entrained flow reactor and vacuum reactor.[86,87] Fluidised bed reactor is most popular due to its easy operation and scale-up but it requires biomass of small particle sizes (<2–6 mm) for effective heat transfer.[75]
- **Controlled pyrolysis temperature**. Biomass pyrolysis for bio-oil production typically operates at 425–600 ˚C.[54] For most woody biomass, the optimal temperature for fast pyrolysis is ~500˚C to maximise bio-oil yield;[75]
- **Short residence time of hot vapour in reactor**. Long residence time (>2 s) can result in significant reduction in bio-oil yield due to bio-oil cracking reactions that can take place under the conditions;[75]
- **Rapid cooling of pyrolysis vapours** for bio-oil collection. The pyrolysis vapour is usually composed of true vapour, aerosol and non-condensable gas.[88] A series of condensers with cooling agents and/or electrostatic precipitation can be equipped to capture pyrolysis vapours.[64,88,89] The non-condensable gas is often recycled to provide heat required in the production process.[90]

A number of pilot or even commercial scale plants for biomass fast pyrolysis have been operating in North America and Europe.[75] Although fast pyrolysis can process various types of biomass, wood is the most commonly used feedstock in large scale productions.[75] In addition, there are also extensive investigations into fast pyrolysis of other biomass source including bark, agricultural residue, and algae, etc.[32,91,92] It is worth noting that algae is a valuable biomass source for biofuel production in the future due to its fast growth rate and low demand for water.[57]

2.3 Characterization, Direct Combustion and Catalytic Upgrading of Bio-oil

Bio-oil, also known as pyrolysis oil or bio-crude,[93] is regarded as a promising substitute for crude oil.[60, 61] However, the chemical composition and physiochemical properties of bio-oil are different from that of petroleum oil. Typical properties of wood bio-oil and heavy fuel oil are listed in Table 2-1. As bio-oil properties are strongly dependent on chemical composition,[94] this section firstly reviews the chemical characterisation of bio-oil. While bio-oil can be used as feedstock for chemical production,[18] this section only reviews bio-oil for fuel applications. The key aspects include bio-oil combustion for heat or power generation, catalytic upgrading of bio-oil to transport fuels and reforming of bio-oil for hydrogen or syngas production. Physical upgrading of bio-oil via mixing with another fuel will be reviewed in section 2.6. Overall fuel applications of bio-oil are illustrated in Figure 2-2 and discussed in Section 2.3.3–2.3.5.

Table 2-1 Typical properties of wood bio-oil and heavy fuel oil[18]

Property	Bio-oil	Heavy fuel oil
elemental composition, wt%		
C	54.0–58.0	85.0
H	5.5–7.0	11.0
O	35.0–40.0	1.0
N	0.0–0.2	0.3
water content, wt%	15.0–30.0	0.1
solids, wt%	0.2–1.0	1.0
ash, wt%	0.0–0.2	0.1
pH	2.5	
density, g/cm^3	1.20	0.94
HHV, MJ/kg	16–19	40
viscosity (cP @ 50 ℃)	40–100	180
distillation residue, wt%	up to 50	1

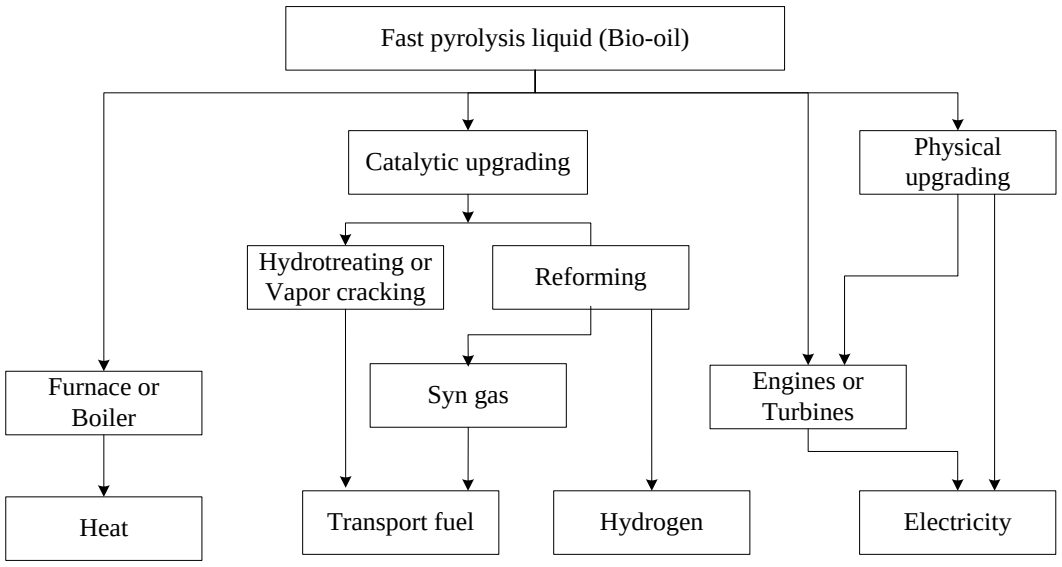

Figure 2-2 Overall fuel applications of bio-oil

2.3.1 Chemical Characterization of Bio-oil

The chemical composition of bio-oil varies significantly, depending on biomass composition (e.g., cellulose, hemicellulose or lignin), pre-treatment (e.g., water or ash content, and particle size), pyrolysis conditions (e.g., temperature, residence time and heating rate) and post treatment (e.g., filtration and condensation), etc.[19] Generally, bio-oil is a complex mixture composed of hundreds of organic compounds, water and solid particles.[22] This subsection discusses the elemental composition, organic composition and their respective characterization methods as follows.

Ultimate Analysis

The major elements in bio-oil are C, H and O, while N, S and metallic elements may present in small quantities.[95,96] Unlike mineral hydrocarbons, bio-oil has a high oxygen content in a range of 35–60% (wet basis).[22] The oxygen is mainly distributed in water but also present in majority of organic compounds in bio-oil.[22] The presence of numerous oxygen-containing compounds in bio-oil is responsible for many problems associated with bio-oil handling and utilization.[96,97] Elimination of oxygen

in bio-oil by catalytic upgrading is therefore an important topic (that will be reviewed in section 2.3.4). Direct determination of oxygen content in bio-oil is technically challenging[98] but oxygen content can be estimated by difference considering the content of C, H, and N (or plus S).[95] Determination of CHN is usually carried out using an elemental analyser according to ASTM D 5291-92.[95] Analysis of S can be accomplished by capillary electrophoresis technique after oxygen bomb combustion of samples according to ASTM D 4239 or by inductively coupled plasma (ICP) analysis following wet digestion of samples.[95,96]

Metal Analysis

Bio-oil contains various inorganic species, particularly alkali and alkaline earth metallic (AAEM) species that can be present in bio-oil at relatively high concentrations.[95] These inorganic species can lead to noxious ash-related issues during thermochemical processes[37] and also act as potential catalysts for bio-oil ageing.[34] Table 2-2 summarises some methods for quantification of inorganic species in biofuels. Basically, the determination method consists of two steps, including pre-treatment that brings samples into solution and analytical measurement that gives element concentration in the solution.[99] Pre-treatment of bio-oil samples before instrumental analysis is a crucial step for accurate quantification of the inorganic species. Commonly used pre-treatment methods include wet digestion (including microwave digestion) and ashing followed by acid digestion (referred to as "ashing–acid digestion"). The advantages and drawbacks of wet digestion and ashing–acid digestion are listed in Table 2-3. Overall, ashing–acid digestion method seems to be a readily available approach, but proper temperature program to minimize volatile loss is warranted for further study, especially for determining inorganic species in liquid fuels. It is within the scope of this PhD study to modify the existing ashing–digestion method for quantification of inorganic (especially AAEM) species in bio-oil and bio-oil-based fuels.

Table 2-2 Some methods for quantification of inorganic species in biofuels

Reference	Sample	Pretreatment method	Analytical method
Abdullah et al., 2010 [27]	bio-oil, biochar, bioslurry	wet digestion using HNO_3–$HClO_4$ acid solution at 150 ℃, then the digested residue was dissolved in HNO_3 for analysis	ICP–AES
Yip et al.,2010[36]	Biochar	combustion in TGA at 600 ℃ followed by acid digestion using hot acid mixture of HF–HNO_3; then the residue was dissolved in 0.02M MSA for analysis	IC
Long et al.,2012[100]	Biochar	microwave digestion using H_2O_2–HF–HNO_3 solution at 180 ℃	ICP–AES
Jendoubi et al, 2011[101]	biomass, biochar, bio-oil	combustion at 500 ℃ for biomass and bio-oil, at 710 ℃ for biochar; then the ash was dissolved in HCl solution and the undissolved residue was burned off at 500 ℃ and 700 ℃ for solid fuel and bio-oil respectively; then the residue was dissolved in HF solution. HCl–HF soluble solution was subjected to analysis	ICP–AES
Naske et al., 2011[33]	Bio-oil	microwave digestion using HNO_3–H_2O_2 acid solution at 275 ℃	ICP–AES
Fahmi et al.,2008[102]	Biomass	dried at 80 ℃ followed by acid digestion using HNO_3–$HClO_4$ solution at room temperature for 2h then HCl solution was added and the mixture was heated at 80 ℃ overnight	ICP–AES
Boucher et al.,2000[103]	bio-oil	ashing based on ASTM D482, then acid digestion using HNO_3–HCl solution and dilution in distilled water for analysis	AAS
Douglas, 1994[104]	bio-oil, biochar	acid digestion using HNO_3–HCl;or fusion followed by dissolution	AAS, ICP–AES
Chiaramonti et al., 2003[105]	bio-oil	temperature-controlled ashing followed by acid digestion using HNO_3–$HClO_4$ solution at 80 ℃	AAS
Henrich et al, 2004[106]	bio-oil	dry combustion, wet digestion, direct dissolution	ICP–AES, AAS

ICP–AES: inductively coupled plasma–atomic emission spectroscopy; IC: ion chromatography; AAS: atomic absorption spectroscopy; TGA: thermogravimetric analyser; MSA: methanesulphonic acid

Table 2-3 Advantages and drawbacks of two pre-treatment methods[99]

Method	Pros	Cons
wet digestion	low volatiles loss due to the low treatment temperature	labor intensive; high background contribution; special equipment required for refluxing the acids mixture
ashing–acid digestion	ability to handle large quantity of sample without intensively increasing treatment time	loss of volatiles as high temperature is used for ashing

Organic Composition

The organic composition of bio-oil is poorly defined. Even though over 400 organic compounds have been identified in bio-oil,[34] there are still ~15 wt% of bio-oil components that cannot be detected by the current analytical techniques.[107,108] The organic compounds in bio-oil can be classified into carboxylic acids, alcohols, aldehydes, ketones, furans, sugars and phenolic compounds etc.[19,34] Major organic compounds identified in bio-oil are listed in Table 2-4.

Gas chromatography coupled with mass spectrometry (GC/MS) is widely used for characterization of volatile organic compounds in bio-oil. In compensation to GC, high performance liquid chromatography (HPLC) can be employed to separate part of the non-volatile compounds in bio-oil for detection. Fourier transform infrared spectroscopy (FTIR) is often used for characterizing functional groups of bio-oil, which can be applied for monitoring chemical reactions occurred during bio-oil ageing.[33] Table 2-5 shows some commonly identified absorption bands in FTIR spectra of bio-oil and corresponding function groups. In addition, in order to obtain more detailed information from the instrumental analysis, fractionation of bio-oil by solvent extraction is often employed based on solubility of bio-oil components in different solvents.[107]

Table 2-4 Typical abundance of major organic compounds in bio-oil[19,32,34,64,109] and possible reactions during storage[34]

Major components	Abundance wt%	Reactions
carboxylic acids	4–15	
formic acid	0.3–9.1	esterification
acetic acid	0.5–12.0	
aldehydes	10–20	
formaldehyde	0.1–3.3	hydration,acetalization,
acetaldehyde	0.1–8.5	polymerization,formation
Ethanedial	0.9–4.6	of resins,oxidation
ketones	1–5	
acetone	2.8	hydration,acetalization,
2-butanone	0.3–0.9	oxidation
alcohols	2–5	
methanol	0.4–2.4	esterification,
ethanol	0.6–1.4	acetalization, oxidation
ethylene glycol	0.7–2.0	
furans	1–6	
furfural alcohol	0.1–5.2	polymerization
furfural	0.1–1.1	
phenolic monomers	2−10	
phenol	0.1–3.8	
2-ethylphenol	0.1–1.3	
4-methyl guaiacol	0.1–1.9	formation of resins
isoeugenol	0.1–7.2	
syringol	0.7–4.8	
phenolic oligomers	15−30	
sugars	20−35	
levoglucosan	0.4–1.4	
fructose	0.7–2.9	
cellobiosan	0.6–3.2	
miscellaneous oxygenates	2–25	
hydroxyacetaldehyde	0.9–13.0	condensation
acetol	0.7–7.4	

Table 2-5 Typical absorption bands in FTIR spectra of bio-oil and corresponding function groups[19,33,110]

Wavenumber cm^{-1}	Functional group	Compound class
3600−3200	O−H stretching; N−H stretching	phenols,alcohols,water,carboxylic acids, amides, amines
2980−2870	C−H stretching	alkanes
1850−1650	C=O stretching	aldehydes,ketones,carboxylic acids, esters
1650−1580	C=C stretching	alkenes
1300–1250	=C−C−O stretching	aromatic ether, carboxylic acid
1200–1100	C−O stretch	secondary alcohols, ether (aliphatic or ring)
1100–950	C=O stretching	primary alcohol

2.3.2 Physicochemical Properties of Bio-oil

Several physicochemical characteristics of bio-oil are summarized in Table 2-6 with detailed discussions listed below:

- **Homogeneity**

Macroscopically, most bio-oils are homogeneous liquids.[22] However, microscopically, bio-oil can be considered as microemulsion.[109] The multiphase structure of bio-oil was attributed to the presence of solid particles, aqueous droplets, waxy materials and heavy compound micelles.[111] Due to density difference, solid particles together with some heavy components in bio-oil may gradually settle at the bottom of vessels during bio-oil storage.[95] Therefore, it is required for homogenization of bio-oil by stirrer or mixer before sampling.[95,112] For the inhomogeneous bio-oil that cannot be homogenized by mechanical forces, it may be homogenized by solvent addition.[112]

Table 2-6 Some characteristics of bio-oil with possible causes and effects[64,88]

Characteristic	Causes	Effects
homogeneity	high water or ash in feed; poor char separation	phase separation; inconsistency in handling, storage and processing
water content	feed water and pyrolysis reactions	decrease in viscosity, stability, density and heating value with increase of water content
solids	incomplete char separation in process; particulates from feed contamination or reactor	sedimentation; blockage; erosion and corrosion
viscosity	chemical composition of bio-oil	fairly high and variable with time; greater temperature influence than hydrocarbons
distillability	reactive mixture of degradation products	bio-oil cannot be completely distilled
acidity	organic acids from biopolymer degradation	corrosion of vessels and pipework
stability	continuation of secondary reactions	slow change in viscosity from secondary reactions; potential phase separation

- **Water content**

Water is the most abundant single component in bio-oil, the content of which is generally in a range of 15–30 wt%.[22,59] The presence of water can be beneficial for reduction in viscosity and pollutant emissions during combustion.[113] However, increase of water content in bio-oil may result in decrease of heating value and even phase separation.[22] Therefore, water content in bio-oil needs to be regulated.[112] As one contributor to the water in bio-oil is the original moisture in feedstock, the moisture content in feedstock biomass is usually controlled to be below 10wt%.[22]

- **Heating value**

Two heating value of fuels may be referred to, i.e. higher heating value (HHV) and lower heating value (LHV). The difference between LHV and HHV is the vaporisation

heat of water during fuel combustion. The LHV of bio-oil (14–18 MJ/kg) is only 40–45% of that of petroleum fuel (41–43 MJ/kg),[22,39] due to the high oxygen and water contents of bio-oil.[39] However, as the density of bio-oil (~1.2 g/cm^3) is higher than that of petroleum oil (0.8–1.0 g/cm^3), the volumetric energy density of bio-oil can account for 50–60% of that of petroleum fuels.[39]

- **Solid and Ash Content**

In biomass fast pyrolysis system, cyclone separators are commonly equipped to separate solid particles from pyrolysis vapours.[22] However, the efficiency of cyclone separator is low for removal of small solid particles (≤10 um).[22] Therefore, there are still considerable amount of fine particles being entrained in the vapours and subsequently condensed in the liquid bio-oil products. Presence of solid particles in bio-oil can have significant negative impacts on bio-oil quality and utilization. For instance, the solid particles tend to agglomerate and settle during bio-oil storage, leading to sampling inconsistency.[39] Besides, high solid content can increase the apparent viscosity of bio-oil thereby resulting in pumping and atomization difficulties.[39] In addition, high concentration of solid particles in bio-oil can contribute to high ash content, which is known to be associated with various problems (e.g., corrosion and deposition) during thermochemical application.[70,114] Therefore, high solid and ash contents in bio-oil are unfavourable. So far, hot vapour filtration seems to be an effective technique to bring down the solid and ash content in bio-oil.[115]

- **Rheological Property and Viscosity**

Viscosity is an important parameter for design and operation of fuel injection and atomization system.[22] For Newtonian fluids, the viscosity remains constant, while viscosity of non-Newtonian fluids may change at different shear rates.[22] The relationship between viscosity and shear rate can be evaluated by rheological studies.

Bio-oil is mostly Newtonian fluid when the temperature is below 80 ℃.[22] However, bio-oil with rich extractives may exhibit non-Newtonian characteristics at low temperature (<46 ℃) or at low shear rate (<50 s^{-1}).[20,111] Typically, the viscosity of bio-oil is in the range of 40–100 cP at a measurement temperature of 50 ℃.[18] Moderate preheating (<90 ℃) of bio-oil before pumping and atomization can reduce the viscosity of bio-oil thereby improving the pumpability and atomization quality.[18]

- **Surface Tension**

Surface tension is another crucial parameter for atomization of liquid fuels.[116] The surface tension of most bio-oil slightly decreases with increasing temperature.[22] At room temperature (~25 ℃), the surface tension of bio-oil varies over a range of 28–40 mN/m,[22] which is higher than that of heavy fuel oil (~23 mN/m @ 25 ℃).[116] This is at least partially due to the high water content of bio-oil considering that surface tension of water is as high as 72 mN/m at 25 ℃.[22]

- **Volatility and Distillation Property**

Bio-oil has a wide range of boiling points because of its complex chemical composition.[18] Generally bio-oil starts boiling below 100 ℃ and stops at about 250–280 ℃ leaving 30–50% residues (weight base) in an atmospheric distillation. The high residue percentage can be attributed to the non-volatile organics condensed in bio-oil (e.g., sugars and oligomeric phenolics) and significant polymerization reactions occurred at elevated temperature during distillation.[18]

- **Acidity and Corrosiveness**

Due to presence of carboxylic acids, the pH and acid number of bio-oil are typically in the range of 2–3 and 36–70 mg NaOH/g respectively.[18,22] For this reason, bio-oil is corrosive to common construction materials such as aluminium, mild steel and

copper.[117,118] Additionally, high temperature or water content was found to exacerbate the corrosiveness of bio-oil.[117] However, stainless steel and various polymers (e.g., polyethylene and polypropylene) are corrosion-resistant materials that can be used for storage and handling of bio-oil.[32,95]

- **Stability**

As bio-oil is not a product of thermodynamic equilibrium, reactions may still take place during storage,[34] resulting in changes in physicochemical properties of bio-oil (e.g., viscosity, homogeneity and acidity) over time. This phenomenon is known as bio-oil ageing. Such ageing may be accelerated at elevated temperatures or in presence of catalysts.[34] For example, it was reported that ageing of a hardwood bio-oil at 90 ℃ for 6 hours was equivalent to ageing at 37 ℃ for 3 months, and the viscosity change after ageing at 80 ℃ for 24 hours was correlated to viscosity change after one year storage at room temperature.[32] Diebold[34] has reviewed the chemical and physical mechanisms of storage stability of bio-oil. Some common reactions responsible for the bio-oil ageing are summarised in Table 2-4 together with major organic components of bio-oil.

2.3.3 Combustion of Bio-oil for Heat and Power Generation

Boilers and furnaces are mostly used for heat generation, while diesel engines and turbines can offer high efficiency for power generation. Despite having relatively low efficiency, boilers and furnaces can operate with various fuels from petroleum distillates to coal/water slurries.[48] It is possible for direct combustion of bio-oil in boilers or furnaces without upgrading. However, application of bio-oil in diesel engines or turbines often requires physical upgrading such as emulsification or solvent addition. Physically upgraded bio-oil fuels including emulsion fuels or fuel blends will be discussed in section 2.6. This subsection only reviews direct application of bio-oil as boiler or furnace fuel.

Commercial combustion of bio-oil for heat generation has been operating for over 10 years at Red Arrow Products in USA.[119] This commercial system uses a 5 MW swirl burner for combustion of bio-oil fractions delivered by a stainless steel nozzle. The emission of such combustion system was reported to be 17, 1.2 and 0.2% of permitted levels for CO, NOx and formaldehyde respectively.[119] Bio-oil combustion in industrial boilers has also been attempted by Stockholm, Oilon and Fortum.[120,121] Researches on bio-oil as a boiler fuel concluded that direct combustion of bio-oil without auxiliary fuel might be feasible with modification of the burner system, improved bio-oil quality (e.g., solid content and ash content lower than 0.1 and 0.03 wt% respectively), and a support fuel at the start up stage.[18,120,122] In general, emission from bio-oil combustion was lower than that from combustion of heavy oils provided that quality bio-oil was properly handled.[18] However, particulate emission might be still beyond the acceptable level for bio-oil combustion.[18] In addition, co-firing of bio-oil with fossil fuels seems to be an appealing option for heat and power generation and has attracted research interests.[123,124]

2.3.4 Catalytic Upgrading of Bio-oil to Conventional Transport Fuel

Upgrading of bio-oil to conventional transport fuel (e.g., diesel, gasoline and kerosene) requires full deoxygenation in combination with conventional refining process. Complete deoxygenation of bio-oil may be achieved by hydrotreating or catalytic vapour cracking as discussed below.

- **Hydrotreating (or hydrodeoxygenation)**

Hydrotreating of bio-oil is performed at moderate temperatures (300–600 ℃) with high hydrogen pressure and catalysts.[18,125] Hydrotreating process removes oxygen as water and results in hydrogenation–hydrocracking of large molecules of bio-oil. Typical catalysts used in hydrotreating process are sulfided CoMo or NiMo catalysts supported on alumina, which are industrial catalysts used for desulfurization or

deoxygenation of petroleum feedstock.[125,126] Elliott et al.[127] have reviewed the developments in hydrotreating of bio-oil. The main challenge of this process is the requirement for high hydrogen pressure which then demands complicated equipment, superior techniques and excess cost.[59,125] Apart from this, catalyst deactivation and reactor clogging can also hinder the implication of this process.[59]

- **Catalytic vapour cracking**

Catalytic cracking of bio-oil is carried out at a temperature range of 350–500 ℃ and atmospheric pressure in presence of catalysts.[125,126] Zeolites catalysts such as ZSM-5 or HZSM-5 are usually employed in this process. Cracking of bio-oil can result in elimination of oxygen as carbon dioxide, carbon oxide, or water. Although hydrogen is not required, the application of this process may be limited by problems such as low hydrocarbon yield, poor product quality and coke formation.[128]

2.3.5 Reforming of Bio-oil for Hydrogen or Syngas Production

Although it is not currently prospective of upgrading bio-oil to conventional liquid transportation fuels by hydrotreating or vapour cracking, another catalytic upgrading technique, bio-oil reforming, has emerged as an alternative pathway of bio-oil fuel application.[18] Table 2-7 summarizes the process conditions, products and limitations of catalytic reforming as well as the aforementioned hydrotreating and vapour cracking techniques. Bio-oil reforming process aims at production of hydrogen or syngas.[18] Extensive investigations have been carried out on hydrogen production via reforming of whole bio-oil or bio-oil aqueous fractions.[129,130] Moreover, syngas produced from bio-oil reforming can be feedstock for synthesizing conventional hydrocarbon fuels or alcohols. The catalysts used for bio-oil reforming are usually precious metals, and the process occurs at high temperatures (600–800 ℃).[64,125] Catalyst deactivation because of coking is one major problem impeding the development of bio-oil reforming.[125,130,131]

Table 2-7 Comparison of three catalytic upgrading techniques of bio-oil

Techniques	Conditions	Products	Limitations
hydrotreating	moderate temperature (300–600 ℃); high hydrogen pressure; sulfided CoMo or NiMo catalysts	naphtha-like liquid products which could be refined in conventional refinery	requirements for complicated equipment, hydrogen supply and excess cost; catalyst deactivation
vapour cracking	moderate temperature (350–500 ℃); atmospheric pressure; zeolite catalysts	liquid products with higher viscosity compared to that from hydrotreating process	low bio-oil yield and quality; catalyst deactivation and coking
reforming	high temperature (600–800 ℃); precious metal catalysts	syngas or hydrogen	catalyst deactivation

2.4 Utilization of Fast Pyrolysis Biochar

Biochar can be produced from fast pyrolysis of biomass with product yield being 10–25 wt%.[54] Effective application of biochar is beneficial for enhancing economic viability and environmental sustainability of biomass pyrolysis process.[65] Biochar from fast pyrolysis process can be used as a fuel for heat and power generation due to its excellent grindability and high energy density.[24,27] Besides, it can be potentially used for soil amendment similar to the application of slow pyrolysis biochar.[132,133] This section discusses the challenges in utilization (especially fuel application) of biochar from fast pyrolysis of biomass.

The main challenge in utilization of fast pyrolysis biochar is associated with the fine particle size distribution, which may cause safety concerns during storage or transportation.[60] For instance, fine biochar powders may spontaneously combust during storage if exposed to oxygen and moisture, and large concentration of biochar

dust in an enclosed area is potentially explosive.[60] Besides, surface application of biochar powders to soils may result in considerable particulate emission which poses a health risk for anyone exposed to the dust.[60]

In addition to safety concerns associated with fast pyrolysis biochar utilization, considerations for fuel application of the biochar also include the reactivity and emission characteristics of biochar during combustion or gasification. Inorganic matters, particularly alkali and alkaline earth metallic (AAEM) species, in biochar are known to be closely related to reactivity and ash-related issues.[36-38] During biomass fast pyrolysis, majority of AAEM species retain in the solid product, i.e. biochar, therefore, the concentration of AAEM species in biochar can be six or seven times higher than that in feedstock biomass.[35, 39] The AAEM species in biochar can act like catalysts for combustion or gasification reactions. The K and Na species appeared to have stronger catalytic effect than the Ca species during steam gasification of biochar.[36] Furthermore, the catalytic effect was also related to the existing form of AAEM species (e.g., in salt form or in organically bound structure).[38] On the other hand, the inorganic matters in solid fuels may cause various notorious ash-related issues during combustion and gasification, including fire-side corrosion,[134,135] ash deposition,[136-138] fine inorganic particulate matter emission,[37,139] and bed agglomeration in fluidized bed operations.[140-143] Therefore, it is crucial to have a thorough understanding of the concentration and composition of inorganic species in biochar for fuel application.

One possible solution to address the issue with fine biochar transportation or storage is suspending biochar into bio-oil to produce bioslurry fuels, which will be reviewed in Section 2.6. It is also within the scope of this thesis to investigate the evolution of inorganic species distribution in biochar after mixed with bio-oil.

2.5 Characterisation and Fuel Application of Glycerol from Biodiesel Production

Glycerol can be sourced from soap or biodiesel industry.[144] Due to its rapid growth, biodiesel industry has become the major driver for glycerol supply.[43,144] In general, approximately 1 kg glycerol can be generated along with production of 10 kg biodiesel by reaction of oil/fat with lower alcohol.[43,49,145-147] The annual global biodiesel production is expected to reach ~37 billion gallons by 2016, leading to an annual production of ~19 million tons of glycerol as a huge accumulated stockpile.[45,148] The management and utilization of such a large-scale waste stream is therefore of great importance to not only the economic performance of biodiesel production value chain but also the environmental sustainability associated with waste disposal.[45-47] Some undesired properties of glycerol are the key challenges in glycerol utilisation. This section reviews the chemical composition and physiochemical properties of glycerol, with emphasis on different pathways for glycerol utilisation as fuel.

2.5.1 Characterization of Glycerol

Chemical composition

The composition of glycerol varies depending on the feedstock, biodiesel production process and refining process of crude glycerol.[48,49] Table 2-8 lists compositions of some glycerol from biodiesel process reported in open literature. Crude glycerol from biodiesel production usually contains less than 88% glycerol,[62,144] with the rest being impurities such as methanol, soap, water, catalysts, salt, fatty acid methyl ester (FAME) and fatty acid. Inconsistency is noted in the chemical compositions of crude glycerol reported in the literature, largely due to some of the biodiesel production processes being not operated in the optimal process configurations. For end use of crude glycerol, it is important to understand how the impurities affect the properties and utilisation of glycerol derived fuels. Such work is included in this PhD thesis.

Table 2-8 Composition of some glycerol from biodiesel production process

Reference	Glycerol	Methanol	Water	Soap	Fatty acid	FAME	Glycerides	Salt
Gupta et al[51]	25−85	up to 25	2−5					
Santibáñez et al[149]	50−60	8−12	2−3	12−16		15−18		
Rehman et al[150]	30	50	2	13				
Liang et al[151]	48.7	22.7	25.6	3.0				
Thompson and He[49]	63−77	23−37						
Valliyappan et al[152]	60	31	7.5					
Pyle et al[153]	56–62	13–28		15–25				
Escribà et al[154]	67.5	30.9	1.6		<1.0		<1.0	
Slinn et al[155]	33	23	3		40			
Hu et al[48]	57.1	11.3	1.0	31.4		0.5	0.4	
	22.9–33.3	10.9–12.6	6.5–18.2	26.2	1.0–1.4	19.3–21.3	1.2–1.6	
	63.0	6.2	28.7					
Hansan et al[156]	76.1	1.8	11.7					
	63.4–64.5	4.7–13.9	0.0–1.0					
Hájek et al[157]	51.3–58.9	1.9–4.6	11.7–14.1	16.8–21.8		6.2–9.3		
Mize et al[158]	50.1–72.3	0.1–0.4	14.1–19.2	<0.5				
Papanikolaou et al[159]	65	3	26					4-5
Chatzifragkou et al[160]	85.0	1.5	6.0		3.0			4.5
	80.1	<0.2	12.9		1.2			5.6
Rywińska et al[161]	92	0.01	6					2-3
Mothes et al[162]	77−90	<2	5−14					1−6

Physiochemical properties

Table 2-9 presents some fuel properties of pure glycerol. The high viscosity and high auto-ignition temperature of glycerol is known to cause difficulties in pumping, atomization, ignition and even flame maintenance.[51,52] The high freezing point may also be problematic if glycerol fuel is used in cold conditions. Because crude glycerol contains various proportions of impurities, the properties of crude glycerol may differ from pure glycerol. For instance, high soap content may increase the viscosity of crude glycerol compared to pure glycerol.[163] Moreover, in presence of high concentration of methanol, the flash point of crude glycerol can decrease significantly, thereby causing major safety concerns during storage and transportation.[164]

Table 2-9 Fuel properties of pure glycerol[165-167]

Properties	Values	Properties	Values
density (25 ℃, g/cm^3)	1.26	auto ignition point (℃)	523
viscosity (25 ℃, cSt)	694.4	boiling point (@ 1 atm, ℃)	290
surface tension (25 ℃, mN/m)	62.87	freezing point (℃)	17
heating value (kcal/mol)	397	flash point (℃)	177

2.5.2 Fuel Application of Glycerol

Purification is an essential step for crude glycerol to penetrate into conventional glycerol markets such as food, cosmetic, pharmaceutical, personal care products or catalytic conversion to chemicals.[43,147] However, purification process is costly and the conventional glycerol markets lack of capability to accommodate the large quantity of crude glycerol emerged.[43] Utilization of crude glycerol as an energy source, on the other hand, seems to be an appealing choice because of several advantages including

drastic volume reduction (glycerol converted into flue gas), easy integration into biodiesel production process (for on-site heat supply hence reducing the dependence on fossil fuel), large-scale application and flexibility to directly accommodate the crude glycerol product without refining.[43,52,53,147,168,169] Current pathways of glycerol utilization are illustrated in Figure 2-3. Even though purified glycerol for energy use is not practical, it is usually adopted for fundamental investigation on fuel application of crude glycerol.

- **Combustion of glycerol or glycerol based fuel mixtures**

Problems associated with direct combustion of glycerol or crude glycerol alone have been reported.[52,170-172] For example, as a result of the high viscosity and ignition temperature of glycerol, incomplete combustion often occurs leading to the formation of unburned toxic products that are of safety and pollution concerns.[51,168] Moreover, high concentrations of inorganic species (primarily Na: ~13,700 ppm, and P: ~1530 ppm) in crude glycerol can be excessive for direct combustion due to ash-related issues.[52,53,168] One possibility to address the challenges with direct combustion of glycerol and mitigate the associated problems is to mix glycerol with other fuels to make fuel blends or emulsions.

Petzer et al.[53] blended glycerol with yellow grease for combustion, although the result was not satisfactory mostly due to the difficulties in maintaining a homogenous mixture. Fernando et al.[47] blended glycerol with gasoline in presence of an amphiphile alcohol produced from catalytic conversion of glycerol. Even though a single phase fuel blend could be obtained, glycerol concentration in the mixture was low (~6 vol%) and a large quantity of alcohol (~60 vol%) was required due to the immiscibility of glycerol with gasoline. Besides, this technique seems difficult to be applied to crude glycerol as catalytic conversion is required to produce the amphiphile alcohol.

Bombos et al[178] investigated the possibility of emulsifying glycerol with fuel oil. Various emulsifiers were attempted and the effects of emulsifier concentration on several fuel properties were reported including flash point, freezing point and viscosity. The stability of the glycerol/fuel oil emulsions was reported to be satisfactory, although the duration of the stability analysis was only 10 hours.[178] Mize et al[164] emulsified crude glycerol with fuel oil for industrial heating. The 7 day stability tests demonstrated the advantage of phase inversion emulsification method and the adverse influence of salt on the emulsion stability.[164] Steady burning of the prepared emulsion fuels was achieved in a waste oil burner.[164] However, the heat output and emission behavior was not characterized. In summary, glycerol based fuel mixtures (fuel blends or emulsions) have great potential for combustion application. However, there is a great need to develop fuel blends of glycerol with alternative fuels, which is also within the scope of this PhD project.

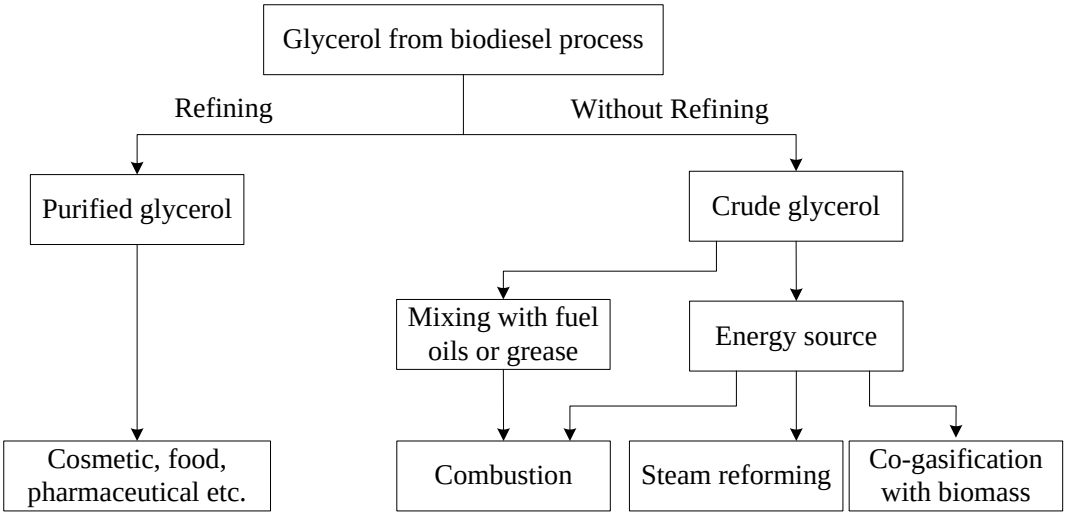

Figure 2-3 Current utilization of glycerol from biodiesel process

- **Steam reforming of glycerol or co-gasification of glycerol–biomass mixtures**

Being oxygenated hydrocarbon, glycerol has a great potential for hydrogen or syngas production via steam reforming or gasification process.[145,152] Most studies investigate on steam reforming using pure glycerol,[152] but recently steam reforming of crude glycerol for hydrogen production has attracted increasing research interests.[155,173] However, deactivation of catalysts was observed during steam reforming of crude glycerol due to the presence of impurities.[156, 166] In addition, some researchers conducted co-gasification for syngas production using mixtures of crude glycerol and biomass.[93, 102, 174] The ratio of crude glycerol to biomass should be considered in order to ensure homogeneous absorption of crude glycerol by biomass.[174] Even though this seems to be a feasible approach for taking up glycerol to subsitue biomass, the mixture is still solid fuel and increased char yield was observed during gasification.[174,175]

2.6 Recent Advancement in Bio-oil-Based Fuel Mixtures

As aforementioned in Section 2.3.3, application of bio-oil in efficient diesel engines or turbines may be achieved by physically upgrading bio-oil to emulsion fuels or bio-oil–solvent fuel blends. Also, slurry fuel prepared from bio-oil and solid fuels (coal or biochar) is also an attractive fuel mixture that can be a near term application of bio-oil. Therefore, this section summarizes the advancement of three bio-oil-based fuel mixtures, i.e. slurry fuel, emulsion fuel and fuel blend.

2.6.1 Bio-oil-Based Slurry Fuel

Slurry fuels can be used in boilers or gasifiers. Key slurry fuel properties include particle size distribution, rheological property and static stability etc.[176] Bio-oil-based slurry fuels found in literature mainly include coal/bio-oil slurry and biochar/bio-oil slurry, recent developments of which are summarised below.

- **Coal/bio-oil slurry.** Although coal/water slurry or coal/oil slurry has been extensively studied,[177-179] investigations on coal/bio-oil slurry are limited. Wang and Song et al.[180] examined the rheological behaviour of coal/bio-oil slurry. The slurry fuels with up to 42 wt% coal loading showed Bingham plastic fluid behaviour.[180] A subsequent study[181] suggested that rheological properties of coal/bio-oil slurry could be affected by several factors including coal rank, solid concentration, particle size distribution and temperature.
- **Biochar/bio-oil slurry.** Biochar/bio-oil slurry, also known as bioslurry, is prepared by suspending fine biochar particles into bio-oil. Such concept was initially attempted by commercial developers such as Karlsruhe ("Bioliq"[106]). Recently, Wu et al.[24,27,28,182] has systematically studied the bioslurry fuels sourced from fast pyrolysis of mallee wood. It has shown that bioslurry can be a promising strategy and potentially make an important contribution to the establishment of a bioenergy industry based on mallee biomass in Western Australia. Additionally, suspending fine biochar particles into bio-oil also addresses the potential issues (dusty and/or spontaneous combustion) associated with biochar direct transport. Studies by this research group have also shown that bioslurry (prepared from biochar and fresh bio-oil or the bio-oil fraction) has good economic viability, small energy and carbon footprints, and desired fuel and rheological properties for combustion or gasification applications. Subsequent work on bioslurry fuel derived from slow pyrolysis or fast pyrolysis of other biomass were also carried out by Caiyot et al.[25] and Trinh et al,[26] with similar findings. Overall, bioslurry intensifies energy density compared to corresponding bio-oil fuel; bioslurry with less than 20 wt% biochar loading exhibits pseudoplastic behaviour; temperature has significant influence on the viscosity and pumpability of bioslurry fuels. Masakazu et al.[183] also conducted gasification using bioslurry with 20 wt% biochar. However, so far little work has been done on the long term stability or ageing of bioslurry fuels.

2.6.2 Bio-oil-Based Emulsion Fuel

Emulsification of bio-oil with diesel or biodiesel may produce emulsion fuels with improved properties. Such emulsion fuels may have potential application in current diesel engines. In this section, both diesel/bio-oil and biodiesel/bio-oil emulsion fuels are reviewed considering fuel preparation, properties and application.

- **Diesel/bio-oil emulsions**

In spite of the mutual immiscibility, bio-oil and hydrocarbons can be emulsified with the aid of surfactants. There have been various studies on emulsification of whole bio-oil or bio-oil aqueous fraction with No.0 or No.2 diesel.[184-187] The produced emulsion fuels are targeted for application in diesel engines. Stability is one of the most important characteristics that need to be considered for emulsion fuels. Ikura et al.[184] found that the emulsion stability of diesel/bio-oil emulsion was significantly influenced by bio-oil concentration, surfactant concentration and power input per unit volume. Chiaramonti et al.[105] employed various commercial surfactants for testing the stability of diesel/bio-oil emulsions and found that emulsions with Uniquma surfactants had the longest stability up to 7 days. Previous studies were also carried out on effects of hydrophile and lipophile balance (HLB) value on surfactant function using Span and Tween series surfactants.[186,188] So far CANMET surfactant has been known as the most cost-effective additive to stabilize diesel/bio-oil emulsion.[184,189] Compared to bio-oil alone, diesel/bio-oil emulsions were also found to have improved other fuel properties (e.g., corrosiveness, cetane number and viscosity), in addition to stability.[17,184] Previous investigations on the combustion of diesel/bio-oil emulsions in diesel engines indicated that erosion of the injectors was a common problem impeding this application.[190-192] It was also reported that reductions in surfactants cost and energy input are of great importance to the development of the emulsion fuels from a practical point of view.[59]

- **Biodiesel/bio-oil emulsions**

Biodiesel as a promising diesel substitute may also be emulsified with bio-oil. Jiang and Ellis[193] suggested that the optimum condition for producing biodiesel/bio-oil emulsion was mixing of bio-oil and biodiesel in volume ratio of 4:6 with addition of 4 vol% octanol as surfactant and stirring at 1200 rpm for 15 minutes at 303 K. The subsequent thermal stability tests indicated that the biodiesel/bio-oil emulsion could be considered as a stable fuel during storage.[194] Prakash et al.[195,196] carried out investigations on application of biodiesel/bio-oil emulsion fuels (with up to 15 vol% bio-oil loading) in diesel engines. The results showed an increase in thermal efficiency, a decrease in emissions of hydrocarbon and CO, but an increase in NO emission compared to operation with diesel fuel alone.

2.6.3 Bio-oil-Based Fuel Blends

Polar solvent addition is considered to be one simple method for upgrading bio-oil.[39] Commonly used polar solvents include methanol, ethanol, acetone and isopropanol etc.[29,39,197] Bio-oil with added polar solvents was found to have improved fuel properties such as reduced viscosity, increased heating value and improved stability.[29,197] Moloodi et al.[198] examined the combustion performance of the ethanol–bio-oil fuel blends in a swirl burner. It was found that the flame stability was improved and emission of CO and hydrocarbon was reduced upon ethanol presence in the fuel blends. Apart from addition of polar solvents, extraction of bio-oil by biodiesel was also attempted to produce biodiesel/bio-oil blends.[199,200] Due to the amphiphilic characteristic, ethanol and butanol were used as co-solvents to produce homogeneous fuel blends together with bio-oil and diesel[189] or biodiesel[201]. Preference of butanol over ethanol as co-solvent was reported as butanol gave a wider composition range of stable fuel blends.[189,201]

2.7 Conclusions and Research Gaps

Based on the above literature review, several key conclusions can be summarized:

- **Firstly**, fast pyrolysis is a promising technology converting bulky biomass into high energy density bio-oil and biochar products. However, some repellent characteristics possessed by bio-oil and biochar have limited their fuel application;
- **Secondly**, among various bio-oil upgrading techniques, catalytic upgrading can enable bio-oil to be used as transport fuel. However, extensive R&D is required before these techniques are economically feasible. Physical upgrading, on the other hand, is considered to be simple ways for adapting bio-oil in diesel engines or turbines. Two physical upgrading methods were reviewed including emulsification of bio-oil with diesel or biodiesel to produce emulsion fuels, and solvent addition to produce bio-oil-based fuel blends;
- **Thirdly**, utilization of fast pyrolysis biochar can encounter transportation or storage difficulties due to the fine particle distribution. Suspending fine biochar particles into bio-oil to prepare bioslurry fuels can be a good solution. Although there have been studies on rheological properties and other fuel properties of the freshly prepared bioslurry, little information is provided on the long term stability of bioslurry during storage. Besides, AAEM species is known to have catalytic function and be in association with ash-related issues during thermochemical processes. However, there is a lack of a suitable method to quantify AAEM species in bio-oil or bioslurry fuels. Establishment of such method can also enable investigation into the distribution of AAEM species during bioslurry storage;
- **Fourthly**, the rapid growth of biodiesel production has resulted in a huge surplus of glycerol, which may cause economic and environmental concerns. Combustion/gasification seems to have wide prospects for taking up the large

quantity waste stream. However, such application may be limited by the undesirable properties of glycerol. Mixing of glycerol with another fuel may alleviate the problems related to direct utilization of glycerol alone. However, appropriate fuel needs to be found for blending with glycerol.

Therefore, further R&D is required to fill the research gaps in application of bio-oil, biochar and glycerol including:

(1) Developing a proper method for quantification of AAEM species in bio-oil and bioslurry fuels. As the existing methods for characterization of AAEM species in solid fuels may not be applicable to liquid or slurry fuels, a suitable method needs to be established for quantifying AAEM species in bio-oil or bioslurry;
(2) Long term stability of bioslurry fuel. As bio-oil is prone to ageing and inherent AAEM species in bio-oil or biochar may act as catalysts to accelerate the ageing process,[34] evolution in fuel properties and distribution of AAEM species should be monitored during long term storage of bioslurry. Further investigation on mechanisms of distribution of AAEM species in bioslurry system is required, as such information can help establish proper methods to control and alleviate unwanted AAEM distribution;
(3) Preparation and properties of fuel blends produced from bio-oil and glycerol. Such fuel blends may have improved properties compared to bio-oil or glycerol alone, and be suitable for application in current stationary engines. It is of great importance to carry out subsequent studies on the effect of impurities in crude glycerol on fuel blend preparation from glycerol and bio-oil. The outcome can provide guidance for blending crude glycerol in bio-oil, thereby enhancing the economic value chain of biodiesel production;
(4) Preparation and fuel properties of slurry fuels produced from biochar and (crude) glycerol/bio-oil blends. Such data is important to assess the viability of integrating bioslurry production process with biodiesel production process;

(5) Preparation and characterization of emulsion fuels from bio-oil and crude glycerol. As soap is a major impurity in crude glycerol and is often known as surfactant,[202] emulsification of bio-oil with crude glycerol seems to be an encouraging option;

(6) Combustion/gasification of slurry fuels (biochar/bio-oil slurry and crude glycerol/biochar/bio-oil slurry) or fuel blends of bio-oil and crude glycerol. As fuel for end use, such investigation is of great importance to understand the combustion or gasification behaviour in practice;

(7) Production of slurry fuels or fuel blends from algae biomass. As a third generation biomass source, algae can be pyrolyzed to produce bio-oil and biochar which can then be used for production of fuel mixtures employing current methodology.

2.8 Research Objectives of Current Study

A list of research gaps in the field have been identified from the literature review, as listed in the previous section. However, with the timeframe of the PhD study, it is impossible to fill all the research gaps. Therefore the scope of this thesis focuses on fuel properties of bio-oil-based slurry fuels with biochar and fuel blends with glycerol. The main objectives of current study are listed as follows:

(1) To develop a method for quantifying AAEM species in bio-oil and bioslurry fuels;

(2) To investigate fuel properties evolution and distribution of AAEM species during long term storage of bioslurry fuels;

(3) To identify the components in bio-oil responsible for the distribution of AAEM during bioslurry storage and provide possible solutions to alleviate the unwanted distribution based on the outcome;

(4) To prepare fuel blends from bio-oil and glycerol and further investigate fuel properties of the fuel blends benchmarked against that of bio-oil or glycerol alone as fuels;

(5) To examine the effect of impurities in crude glycerol on blending of bio-oil and glycerol and provide further guidance on integration of such blending process into biodiesel production process.

CHAPTER 3 RESEARCH METHODOLOGY AND ANALYTICAL TECHNIQUES

3.1 Introduction

This chapter describes the overall research methodology employed to achieve the thesis objectives outlined in Chapter 2. Details of experimental and analytical techniques are given in the following sections.

3.2 Methodology

Two fuel mixtures are considered in this thesis, i.e. bioslurry fuel prepared from bio-oil and biochar, and fuel blend prepared from bio-oil and glycerol. A series of systematic experiments were carried out, including:

- Pyrolysis of biomass in a fluidized bed reactor or a drop-tube/fixed bed reactor system to produce biochar for preparation of bioslurry fuels;
- Preparation of fuel mixtures with different liquid to solid ratio or different bio-oil proportion;
- Ageing of the fuel mixtures at room temperature for long period or at elevated temperature for short time;
- Characterization of the fuel mixtures using an array of analytical instruments, including rheometer, ion chromatography and Karl Fisher titrator etc.

In this research, experiments or instrumental analyses were replicated to ensure reproducibility of results. The overall methodology for achieving the research objectives is illustrated in Figure 3-1 with detailed explanations in the following sections.

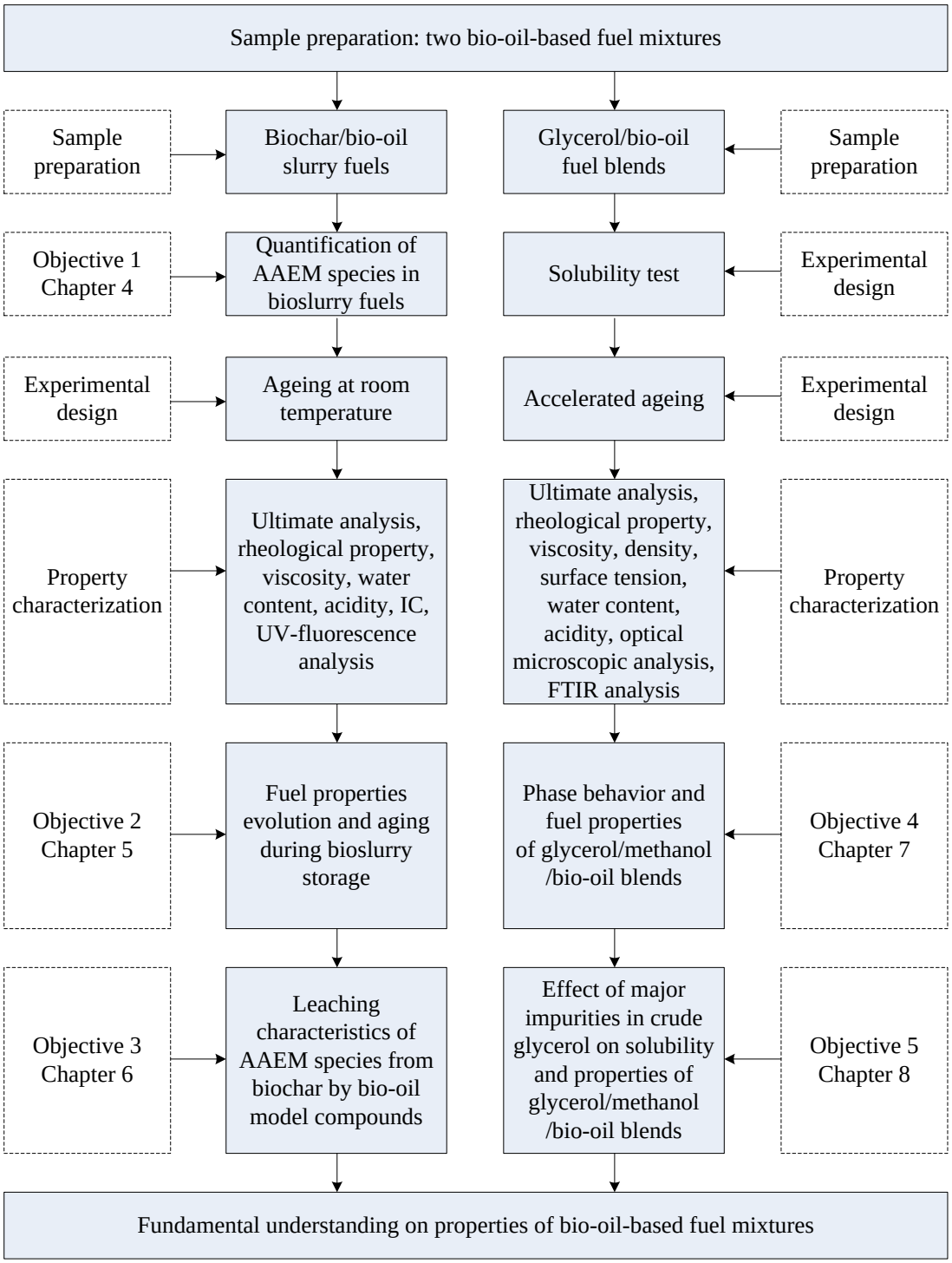

Figure 3-1 Research methodology and linkage with the research objectives (see Section 2.8) to be achieved in this PhD study

3.2.1 A Method for the Quantification of Alkali and Alkaline Earth Metallic (AAEM) Species in Bioslurry Fuels

The biochar samples were produced from pyrolysis of pine wood in a fluidized bed reactor (see Section 3.3.1 and 3.3.3). Series of bioslurry fuels were prepared from two bio-oils and the produced biochar (Section 3.3.1). The ultimate and proximate composition of the bio-oil and biochar samples were analysed according the the method detailed in Section 3.4.1. Several fuel properties of bio-oil samples were analysed, including viscosity (Section 3.4.3), total acid number (TAN), water content and solid content (Section 3.4.4). All the bioslurry and blank bio-oil samples were subjected to quantification of AAEM species via existing and newly developed ashing−digestion−IC methods and microwave digestion–ICP method (Section 3.4.2). The results of this work are shown in Chapter 4.

3.2.2 Evolution of Fuel Properties and Aging during Bioslurry Storage

The biochar samples used in this set of work and subsequent work in Chapter 6 were produced from pyrolysis of pine wood biomass in a drop-tube/fixed bed reactor (see Section 3.3.1 and 3.3.3). It was reported previously that the soot-like solid particles (typically with a content of <0.5 wt%) in fast pyrolysis bio-oil may experience agglomeration during bio-oil cold storage.[203] Therefore, to eliminate this effect, two filtered bio-oils (Section 3.3.1) were mixed with the biochar to prepare bioslurry fuels used in this work. The obtained bioslurry fuels were stored at room temperature for up to 29 days. During this storage period, bio-oil was separated from bioslurry at designated time (Section 3.3.2). The separated bio-oil together with the blank bio-oil samples were characterized using various analytical techniques detailed in Section 3.4. For instance, a rheometer was used to analyse the rheological properties and viscosity of bio-oil samples (Section 3.4.3). The water content and total acid number (TAN) were analysed using Karl fisher titrator

and acid–base titrator respecively (Section 3.4.4). Quantification of AAEM species in biochar was carried out using the existing ashing−digestion−IC methods (Section 3.4.2). The AAEM species in bio-oil samples were determined using the method developed in Chapter 4. Analysis of AAEM species in biochar and bio-oil samples was used to examine the distribution of AAEM species in bioslurry during storage. The results and discussion for this work are covered in Chapter 5.

3.2.3 Leaching Characteristics of Alkali and Alkaline Earth Metallic (AAEM) Species from Biochar by Bio-oil Model Compounds

The results in Chapter 5 showed an increase of AAEM species in bio-oil phase, implying that the AAEM species were leached out from biochar by bio-oil during bioslurry storage. In Chapter 6, the leaching mechanism was investigated using several bio-oil model compounds. A series of mixtures were prepared, including biochar–bio-oil model compounds mixtures and biochar–bio-oil water soluble fraction mixtures. These mixtures were stored at room temperature for up to 7 days, and then the liquid phase was separated and collected for subsequent analysis, including quantification of AAEM species following the method developed in Chapter 4 and UV–florescence spectropic analysis (Section 3.4.7). Chapter 6 explains the results and discussions for this work.

3.2.4 Phase Behaviour and Fuel Properties of Glycerol/Methanol/Bio-Oil Blends

To achieve the fourth objective outlined in Section 2.8 of Chapter 2, a series of systematic experiments were conducted. Firstly, the solubility of glycerol in bio-oil was examined using optical microscopic analysis (Section 3.4.5). Methanol was added to aid the dissolution of glycerol in the bio-oil. Therefore, a series of glycerol/methanol/bio-oil blends were prepared. Secondly, the selected fuel blends were subjected to various analyses, including density and surface tension (Section 3.4.6), elemental analysis (Section 3.4.1) and viscosity (Section 3.4.3), etc. On the

basis of the solubility and fuel properties of the glycerol/methanol/bio-oil blends, feasible composition range was recommended and two fuel blends in this range were selected for subsequent accelerated ageing evaluation (Section 3.3.2). Chapter 7 presents the results and discussions for this work.

3.2.5 Effect of Major Impurities in Crude Glycerol on Solubility and Properties of Glycerol/Methanol/Bio-oil Blends

To investigate the influence of impurities in crude glycerol on solubility and properties of glycerol/methanol/bio-oil blends, four major impurities were selected and mixed with glycerol separately or together to prepare a set of impurity-containing glycerol mixtures including formulated crude glycerol. The effect of these impurities on the solubility of glycerol in bio-oil was examined by the minimum methanol percentage required for obtaining homogenous blends. Selected homogenous fuel blends with fixed methanol and bio-oil composition were subjected to accelerated ageing experiments (Section 3.3.2). Various fuel properties characterized in this study included viscosity, water content, TAN, and elemental composition etc. The detailed results are reported in Chapter 8.

3.3 Experimental

3.3.1 Sample Preparation

Biomass and Biochar. A batch of dry pine wood chips was kindly supplied by WA&J King Pty Ltd (Western Australia). The received pine wood biomass was then cut and sieved into size fractions of 4–6 mm and 1–2 mm. The prepared biomass sample was sealed in plastic bags and stored in a freezer under -4 °C before pyrolysis for biochar production. Two biochar samples were prepared in this PhD project as seen in Figure 3-2. The one used in Chapter 4 was produced in a fluidized bed reactor system using 4–6 mm biomass. The other biochar sample used in Chapter 5

and 6 was prepared in a drop-tube/fixed bed reactor system using 1–2 mm biomass. Both biochars were produced at ~500 °C and corresponding reactor systems used for biochar production can be seen in Section 3.3.3. The collected biochar samples were ground using a ball mill (Retsch MM400) for 8 min at a frequency of 15 Hz and then sieved to size less than 75 μm for further experiments.

Bio-oil and Bioslurry. Two bio-oil samples (referred to as "bio-oil A" and "bio-oil B") were sourced from two commercial suppliers, where pine wood samples available to the suppliers were used as feedstocks for producing the bio-oils under fast pyrolysis condition at ~500 °C. The received bio-oil samples were stored in fridge at ~4 °C prior to use. Detailed bio-oil allocation in this thesis is sketched in Figure 3-2. As-received bio-oil was used throughout the thesis except for experiments in Chapter 5, where both bio-oil A and bio-oil B were filtrated through a 0.45 μm PVDF syringe filter for experiments. Bioslurry samples were prepared by mixing the ground biochar particles (with size <75 μm) into the bio-oil samples following a method developed previously.[27] Bioslurry samples prepared using bio-oil A or bio-oil B were referred to as "bioslurry A, xx% biochar" or "bioslurry B, xx% biochar" (xx% represents the weight percentage of biochar in bioslurry). Due to experimental limitations, it is noted that the two bio-oil samples and the biochar sample were not produced from the same pine wood sample. Nevertheless, this fact should not influence the conclusions drawn in this study. In addition, as bio-oil property is prone to change over time, characterization of the bio-oil samples was carried out prior to experiments and the results are presented in each chapter.

Other chemicals used in this study. Glycerol (G5516), formic acid (399388), phenol (328111), guaiacol (G5502) and sodium oleate (26125) were sourced from Sigma Aldrich. High-purity analytical-grade methanol (≥99.8%), acetone (≥99.8%), acetic acid (≥99.7%), NaOH powder and NaCl powder were purchased from Chem–Supply.

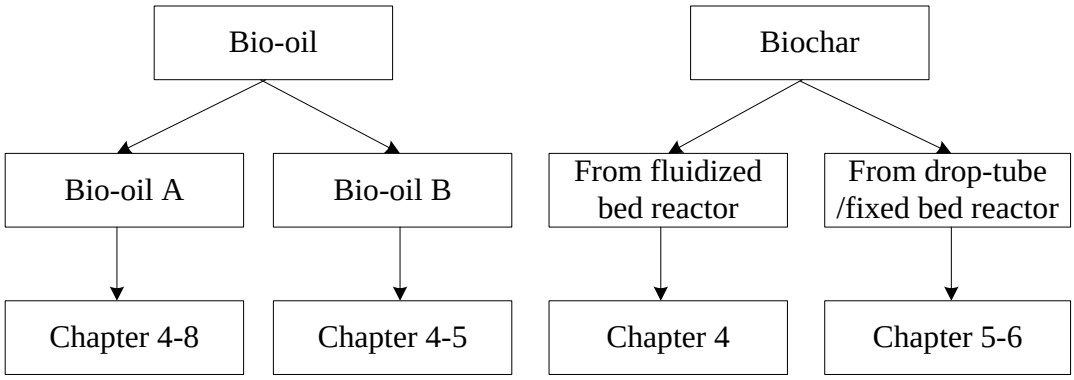

Figure 3-2 Allocation of bio-oil and biochar samples in this thesis

3.3.2 Ageing, Leaching and Accelerated Ageing Experiment

A**ging experiment** in Chapter 5. Each bioslurry sample (bioslurry A, 10% biochar and bioslurry B, 10% biochar) was evenly divided into eight containers. Equal quantity of bio-oil A and bio-oil B was also dispensed into four containers as blanks (referred to as "bio-oil A, blank" and "bio-oil B, blank") for comparison. During the ageing experiments, for each bioslurry (or bio-oil) sample, sampling was done after designated ageing periods (i.e. 20 minutes, 40 minutes, 2 hours, 8 hours, 1 day, 5 days, 15 days and 29 days). For each sample collected, the bio-oil phase was then separated via centrifugation at 4500 rpm for 10 minutes and subsequently filtered through a 0.45 μm PVDF syringe filter. The filtered bio-oil samples were then stored below 4 ℃ for subsequent analysis. As control group, the bio-oil blanks were undergone the same process at sampling times of 20 minutes, 5 days, 15 days and 29 days.

Leaching experiment in Chapter 6. Selected bio-oil model compounds (individual chemical or solution) as well as the water soluble fraction of bio-oil A was mixed with biochar in a mass ratio of 20:1 if not specified. The mixtures were then sealed in clean containers at room temperature for up to 7 days. After the leaching experiment was completed, the mixture was separated by a syringe with a 0.45 μm filter and the liquid phase was collected for subsequent analysis. The bio-oil water soluble fraction was

obtained by water addition into bio-oil in a mass ratio of 1:1 and collection of the upper layer after phase separation. Another two bio-oil water soluble fraction to biochar ratios (i.e. 29:1 and 40:1) were also employed for comparison with the ratio of 20:1. Chapter 6 provides more details about mixture composition and liquid to solid ratios for the leaching study.

Accelerated ageing experiment in Chapter 7 and Chapter 8. The accelerated ageing experiments of the bio-oil-based fuel blends were conducted according to a method stated elsewhere.[33,91] Briefly, selected samples were sealed in clean Pyrex glass containers and placed in an oven at 80 ℃ for 24 h, which is equivalent to aging at room temperature for one year.[32] Upon the completion of the experimental program, the samples were cooled rapidly in an ice bath. The mass of these samples before and after heating were then recorded to ensure insignificant volatile loss during heating. The aged samples together with the corresponding control samples were then subjected to subsequent analysis (i.e. viscosity, water content and acidity).

3.3.3 Reactor Systems for Pyrolysis Experiment

Pyrolysis in a fluidized bed reactor. Pyrolysis of 4–6 mm pine wood samples were carried out using a laboratory-scale fluidized-bed reactor (see Figure 3-3a) similar to the one used previously.[204] Briefly, ~500 g of high-purity silica sand (size of 125–355 μm) was first loaded into the reactor and preheated to the pyrolysis temperature (i.e. 500 ℃). Argon was used as a carrier gas, and its flow rate was adjusted to maintain proper fluidization of bed materials. The feeding rate of pine wood particles was adjusted at ~1 g/min. Once feeding was completed, the reactor was lifted out of the furnace and cooled to room temperature, with argon continuously passing through the reactor. The biochar and sand particles were then collected from the reactor and gently sieved using a 1 mm screen to separate the biochar from the sand.

Pyrolysis in a drop-tube/fixed bed reactor. A lab-scale drop-tube/fixed-bed

pyrolysis reactor (see Figure 3-3b) similar to the one used in a previous study [205] was used for producing biochar for studies in Chapters 5 and 6. Briefly, the quartz reactor was preheated to a pyrolysis temperature of 500 ℃, with a stream of ultrahigh-purity argon (purity > 99.999%) flowing through the reactor at 1 L/min. The biomass sample (1–2 mm) was fed into the reactor at a feeding rate of ~1 g/min, and the reactor was further held at the pyrolysis temperature for 10 min. Once the pyrolysis was completed, the reactor was lifted from the furnace to cool rapidly (with the ultrahigh-purity argon continuously flowing through the reactor) to room temperature under ambient conditions for sample collection.

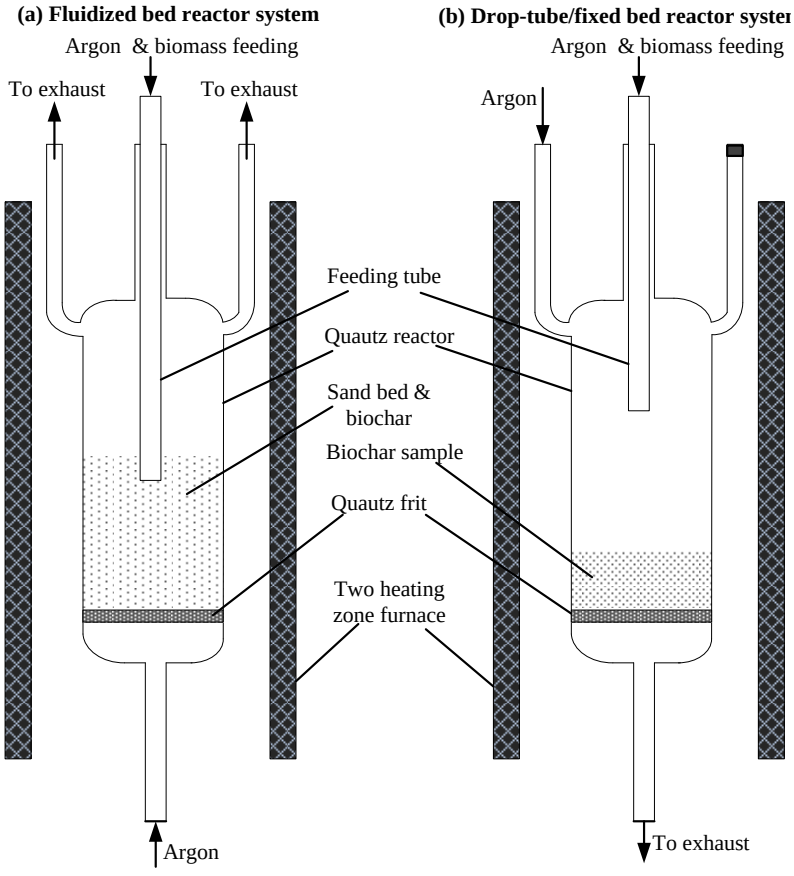

Figure 3-3 (a) Fluidized bed reactor system and (b) drop-tube/fixed bed reactor system

3.4 Instruments and Analytical Techniques

3.4.1 Proximate and Ultimate Analysis

The ultimate analysis of bio-oil or biochar samples was conducted using a CHN/O elemental analyzer (PerkinElmer 2400 series II model). The proximate analysis of biochar samples was conducted using a thermogravimetric analyzer (TGA; Mettler TGA/DSC 1 STAR model), following the procedure described in ASTM E870-82.[206]

3.4.2 Quantification of Alkali and Alkaline Earth Metallic (AAEM) Species

Existing ashing–digestion–IC method. This method has been extensively applied for quantification of AAEM species in low-rank solid fuels such as brown coal, biomass and biochar.[36,207-209] Briefly, a known amount of a sample was placed in a platinum (Pt) crucible which was then subjected to a temperature-time program in air. The program includes multiple slow-heating and holding steps from room temperature to a termination temperature of 600 °C, originally purposely designed for biomass and biochar. The resulted ash was then digested in a mixture of HF acid and HNO_3 acid (at a volume ratio of 1:1) at 120 ^{o}C for at least 12 hours. The solution after digestion was evaporated to remove residue acids and then dissolved in 20 mM methanesulfonic acid (MSA) for quantification of AAEM species using an ion chromatography (IC) (model: ICS 3000, column: CS12A, eluent: 20 mM MSA). This method was used for quantifying AAEM species in biochar samples throughout this study.

New evaporation–ashing–digestion–IC method. This method is designed and developed based on the existing ashing–digestion–IC method. It deploys an additional step designed for the progressive evaporation of bio-oil vapors as a mean to avoid the loss of AAEM species that otherwise would occur during the ashing step. The establishment of this method is given in Chapter 4. This method was adopted for subsequent quantification of AAEM species in bio-oil or liquid samples.

Existing microwave–ICP method. This method combines microwave digestion of a sample to produce a solution and quantification of AAEM species in the solution via inductively coupled plasma−atomic emission spectrometry (ICP–AES). The analyses were conducted by ChemCentre (Perth, Australia,). Briefly, ~0.2 g sample was mixed with 20 mL mixture of HNO_3 acid, HCl acid, and H_2O (at a volume ratio of 10: 0.5: 9.5), and digested following modified EN13805:2002/USEPA 3052 method.[210] The digested solution was filtered (if cloudy) before being injected into ICP−AES for analysis. This method was only used in Chapter 4.

3.4.3 Rheological Property and Viscosity

The rheological properties of bio-oil samples were characterised using a rheometer (model: Haake Mars II) fitted with a cone-plate C35/4 sensor system. A sample size of ~0.8 mL was used for each measurement. Steady shear tests were conducted to investigate the flow characteristic of bio-oil samples. Briefly, for a bio-oil sample, the shear rate was ramped up to 500 s^{-1}, held for 30 s and then reduced down to 0 s^{-1} in order to study the time dependent characteristics of the sample. The viscosity was averaged from the data obtained in a range where the samples showed Newtonian behaviour. The measurement temperature was controlled by a Haake Thermocontroller TC501.

3.4.4 Solid content, Water Content and Acidity

The solid content of bio-oil was determined based on a procedure modified from VTT publication 306.[211] Briefly, ~2 g bio-oil was dissolved in methanol and filtrated using three layers of filter paper (MN615, 4 μm pore size). The mass of solid retained on the filter paper was then used to determine solid content of the bio-oil.

The water content of bio-oil was analysed using Karl-Fischer titration method detailed elsewhere.[95] Briefly, ~0.25 g bio-oil was dissolved in a mixture of Hydranal methanol

and chloroform (volume ratio: 3:1), and titrated by Hydranal Composite 5K in a titrator (model: Mettler V30). The Hydranal working medium K was added to avoid fading of titration end point.

The acidity of bio-oil was characterized by total acid number (TAN). To quantify the TAN of bio-oil samples, ~1 g bio-oil was dissolved in 50 mL acetone and then titrated by 0.1 M sodium hydroxide solution using MEP Oil Titrino plus 848.[212-214]

3.4.5 Solubility of Liquid Fuel Blends and Optical Microscopic Analysis

Solubility of glycerol or impurity-containing glycerol in the bio-oil was examined by optical microscopic analysis. Briefly, glycerol or impurity-containing glycerol was blended with the bio-oil sample, followed by gradually adding methanol until a homogenous phase similar to that of the bio-oil was observed under an optical microscope (model: Olympus SL 60/61). As bio-oil itself is a micro emulsion[111] and the dark colour can mask the phase separation line, solubility of the (impurity-containing) glycerol–bio-oil mixtures is determined by obtaining homogenous microscopic picture similar to that of the bio-oil. The solubility tests were performed at room temperature (~25 ℃), and a magnetic stirrer was used to ensure immediate and complete mixing of these components. The relative standard error for this solubility determination method is within 5% of methanol composition in the blends (on a weight basis).

3.4.6 Surface Tension and Density

The surface tension of liquid fuel samples was determined following Wilhelmy method on a surface tensiometer (KSV Sigma 701) fitted with a round platinum rod probe (diam. 1 mm).[28] The bulk density was measured by a pycnometer (25 mL) with standard deviations less than 1%. Both surface tension and density measurements were carried out at room temperature (~25 ℃).

3.4.7 FTIR and UV-Fluorescence Spectroscopic Analysis

Fourier transform infrared (FTIR) spectroscopic analysis was performed to analyse the functional groups of selected samples using an attenuated total FTIR spectrometer (Perkin-Elmer Spectrum 100). Peak height ratios were calculated for quantitative analysis according to a method detailed elsewhere.[33]

The ultra violet (UV)–fluorescence spectroscopic analysis was carried out using a spectrometer (model: PerkinElmer LS55) in a synchronous scan mode with a slit width of 2.5 nm and a constant energy difference of –2800 cm^{-1} following a method used previously.[215]

3.5 Summary

Bioslurry samples were prepared from bio-oil and biochar derived from fast pyrolysis of pine wood biomass. A suitable method for quantification of AAEM species in bio-oil and bioslurry was established and applied for subsequent analysis of AAEM species in bio-oil samples. Ageing of bioslurry and leaching of biochar by bio-oil model compounds were carried out at room temperature for designated period to investigate evolution of fuel properties and distribution of AAEM species during bioslurry storage. In addition to bioslurry samples, fuel blends prepared from bio-oil and glycerol in presence of methanol and other impurities in crude glycerol were also studied in order to provide guidance for integration of the fuel blending process with biodiesel production process. Accelerated ageing tests were conducted for the fuel blends to investigate the long term stability. Rheological properties and other fuel properties of the fuel samples were characterized using the analytical techniques describe in section 3.4, including viscosity, water content, acidity, density and surface tension etc. The fundamental understandings on the quality of the bio-oil derived slurry fuel and fuel blend were then achieved.

CHAPTER 4 A METHOD FOR THE QUANTIFICATION OF ALKALI AND ALKALINE EARTH METALLIC SPECIES IN BIOSLURRY FUELS

4.1 Introduction

As reviewed in Chapter 2, fast pyrolysis technology converts biomass into high-energy-density fuels including biochar and bio-oil.[3,4,6,216-218] A near-term strategy for bio-oil application is to produce bioslurry fuels via suspending fine biochar particles into bio-oil. Such a concept not only intensifies energy density of bio-oil, but also addresses the potential issues (dusty and/or spontaneous combustion) associated with biochar direct transport. Bioslurry was previouly attempted by commercial developers (e.g., Karlsruhe[23]) and subsequently investigated into rheological properties and other fuel properties (e.g., viscosity, surface tension and static stability).[25-28] As a mixture of biochar and bio-oil, bioslurry contains abundant alkali and alkaline earth metallic (AAEM, mainly Na, K, Mg, and Ca) species. Transformation of these ash-forming species in fuels is important to reactor designs and product qualities,[82,219-221] and responsible for various notorious ash-related issues during combustion and gasification.[37,134-143] It is therefore of great significance to accurately quantify AAEM species in bioslurry fuels.

Some methods for quantification of inorganic (including AAEM) species in biofuels are listed in Table 2-2 in Chapter 2. One approach for quantification of ash-forming species in fuels includes fuel oxidation (or ashing) to convert these species to ash, followed by acid digestion of the ash into solution then quantification using analytical instruments such as ion chromatography (IC) and/or inductively coupled plasma−atomic emission spectrometry (ICP–AES). In these methods (hereafter

referred to as "ashing–digestion–IC" or "ashing–digestion–ICP" methods), fuel sample ashing deploys a temperature-time profile using slow heating (up to 10 ^{o}C/min), multi-step holding and low temperatures (up to 600 ^{o}C) to avoid sample ignition, hence, reserve ash-forming species in the ash product. The subsequent ash digestion uses a mixture of hydrofluoric acid (HF) and nitric acid (HNO_3). These enable complete oxidation, ~100% retention of ash-forming species in ash and complete ash digestion. Such methods have been proven to be useful in accurate quantification of inorganic (including AAEM) species in solid fuels such as brown coal, biomass, and biochar.[36,207-209] However, it is still questionable whether such methods can be adopted to bioslurry because of the introduction of bio-oil into the fuel. It is doubtful if 100% of ash-forming species in bio-oil can be retained in the ash product after ashing using the ashing program because bio-oil is prone to ignition and the vapors produced upon bio-oil heating may also carry biochar particles out of the ashing crucible during ashing. On the other hand, because of its simplicity and easy operations, microwave digestion[33,222] has been widely used for converting bio-oil into a suitable solution. The solution was then subsequently subjected to ICP–AES analysis for quantification of ash-forming species in bio-oil. However, such a method (hereafter referred to as "microwave–ICP" method) may not be applicable to quantify ash-forming species in bioslurry because microwave digestion is probably not able to completely digest the solid biochar particles present in bioslurry.

Therefore, this chapter aims to examine whether these existing methods for quantification of ash-forming species in solid fuels can be directly applied to bioslurry fuels. The experimental program for such assessment is focused on the suitability of the ashing–digestion–IC method and microwave–ICP method for quantifying AAEM species in bioslurry. Furthermore, a new method was then developed for quantifying AAEM species in bioslurry fuels via incorporating an additional progressive evaporation step considering the presence of bio-oil in bioslurry. Table 4-1 shows the properties of bio-oil A, bio-oil B and the biochar sample used in this chapter.

Table 4-1 Properties of the bio-oil and biochar used in Chapter 4

Samples	Bio-oil A	Bio-oil B	Biochar
Proximate analysis			
Water content (wt%, ar[a])	24.4	27.7	1.4
Ash (wt%, db[b])	nd[c]	nd[c]	9.9
Volatile matter (wt%, db[b])	nd[c]	nd[c]	18.9
Fixed carbon (wt%, db[b])	nd[c]	nd[c]	71.2
Ultimate analysis (wt%, daf[d])			
C	42.64	40.48	86.21
H	7.55	8.28	3.19
N	0.22	0.30	0.16
O[e]	49.59	50.94	10.44
Viscosity (25^{o}C, mPa s)	112.5	57.3	
Solid content (wt%, ar[a])	0.01	0.1	
TAN[f] (mg NaOH/g bio-oil)	49.7	46.2	

[a] as received basis. [b] dry basis. [c] not determined. [d] dry and ash free basis. [e] by difference. [f] total acid number.

4.2 Evaluation of the Ashing–Digestion–IC Method for Quantifying AAEM Species in Bioslurry Fuels

Table 4-2 presents data on the concentrations of AAEM species in bioslurry fuels quantified by the ashing–digestion–IC method and the microwave–ICP method, along with the data for the bio-oil and biochar samples using the same methods. Three important findings can be observed. First, the concentrations of AAEM species (particularly K and Ca) in biochar quantified by the microwave–ICP method are considerably lower than those determined by the ashing–digestion–IC method. It was demonstrated that the ashing–digestion–IC method is able to accurately quantify AAEM species in brown coal, biomass and biochar.[36,207] Therefore, such reduction in the concentrations of AAEM species shows that the microwave–ICP method underestimates the contents of AAEM species in biochar, possibly as a result of incomplete oxidation of biochar particles during microwave digestion under the experimental conditions. To prove this point, the solution obtained from biochar microwave digestion was evaporated at 60 ^{o}C to obtain a solid residue that was then

subjected to TGA analysis under air or argon atmosphere according to a procedure detailed elsewhere.[223] Figure 4-1 presents the thermogravimetric (TG) curve and derivative thermogravimetric (DTG) curve of the solid residue, showing that the weight loss in air in temperature range of 350–530 ^{o}C is substantially higher than that in argon. This suggests the presence of un-oxidized carbonaceous materials[223] in the solid residue. The incomplete oxidation of biochar by microwave digestion can be attributed to the high carbon content in biochar (see Table 4-1). The other is the absence of HF acid during microwave digestion. It is known that HF acid is essential to the complete digestion of Si-containing species when these compounds are present in samples.[224,225] Therefore, the microwave–ICP method underestimates the concentrations of AAEM species in biochar (hence, bioslurry fuels) because of incomplete oxidation of biochar particles and/or incomplete digestion of AAEM species associated with Si-containing species.

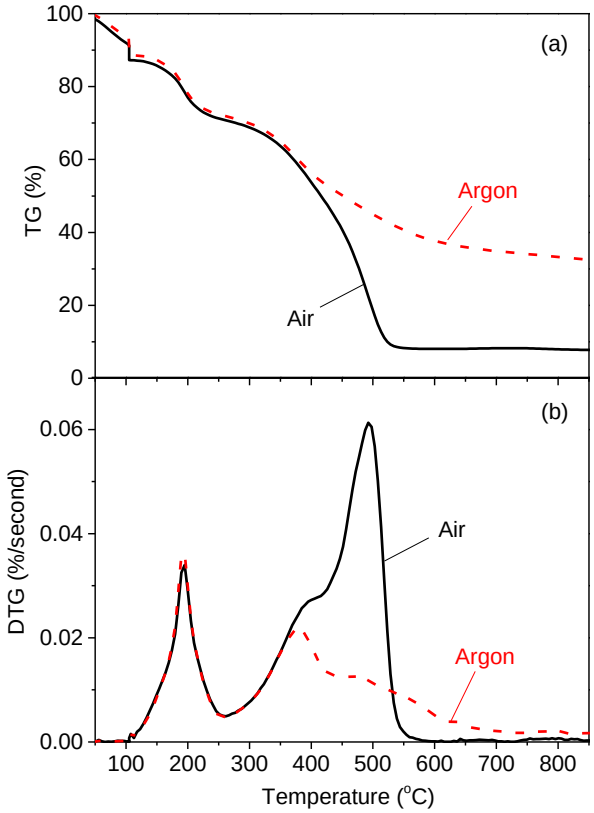

Figure 4-1Thermogravimetric (TG) curve (a) and derivative thermogravimetric (DTG) curve (b) of solid residue after evaporating microwave digestion solution of biochar

Second, the Na concentration in the two bio-oil samples is below limitation of quantification (LOQ) of the microwave–ICP method, from which the concentrations of K, Mg, and Ca obtained are in reasonable agreement with those from the ashing–digestion–IC method. The results show that although microwave digestion is unable to completely oxidize biochar, it can completely oxidize and digest the two bio-oil samples. Indeed, this is evidenced by the fact that the digested solution is clear[33] and no solid residue can be observed after being evaporated at 60 ^{o}C. The suitability of microwave digestion for bio-oil samples was reported previously.[33,222] This is understandable because bio-oil has a low carbon content and a high oxygen content (see Table 4-1). The microwave digestion is also conducted in a close system, so that the loss of AAEM species during digestion is minimized. In addition, the good agreement on the contents of AAEM species (mainly K, Mg, and Ca) obtained from the two methods implies that the ashing–digestion–IC method can also reasonably quantify the AAEM species in bio-oil. The loss of AAEM species (if any) from bio-oil during ashing process is therefore negligible, which provides the foundation of using the ashing–digestion–IC method or its improved method to quantify the AAEM species in bioslurry fuels.

Table 4-2 Concentrations of the AAEM species in biochar, bio-oil and bioslurry fuels by different quantification methods

Concentration (ppm)		Fuels						
		Biochar	Bio-oil A	Bio-oil B	Bioslurry A, 5% biochar	Bioslurry A, 10% biochar	Bioslurry A, 20% biochar	Bioslurry B, 10% biochar
Na	Method 1[a]	80 ±3	<10	<10	<10	<10	15 ±1	16 ±2
	Method 2[b]	111.0 ±3.0	0.7 ±0.1	10.0 ±0.5	5.8 ±0.2	11.2 ±0.6	5.5 ±0.6	11.6 ±1.5
	Method 3[c]		0.8 ±0.1	10.2 ±0.1	6.1 ±0.1	12.6 ±0.2	24.9 ±0.6	21.2 ±0.1
K	Method 1[a]	2850 ±50	13 ±1	38 ±2	175 ±15	360 ±10	630 ±10	365 ±45
	Method 2[b]	3766.7 ±3.0	13.2 ±0.2	45.1 ±0.9	195.2 ±11.1	366.9 ±1.6	191.4 ±13.6	256.7 ±19.3
	Method 3[c]		13.3 ±0.1	45.9 ±0.2	206.0 ±0.8	405.6 ±0.4	783.5 ±4.1	433.0 ±4.2
Mg	Method 1[a]	1100 ±10	3 ±1	32 ±1	66 ±7	135 ±5	235 ±5	150 ±20
	Method 2[b]	1316.9 ±2.0	2.5 ±0.2	33.2 ±0.8	66.4 ±4.6	126.7 ±0.7	62.9 ±8.2	91.8 ±7.4
	Method 3[c]		2.5 ±0.1	33.9 ±0.1	69.2 ±0.8	141.0 ±0.1	270.0 ±1.3	169.2 ±1.5
Ca	Method 1[a]	2950 ±50	21 ±2	187 ±7	175 ±15	360 ±20	712 ±65	578 ±53
	Method 2[b]	3694.5 ±11.9	17.5 ±3.4	186.4 ±8.9	180.2 ±13.9	336.1 ±1.1	172.1 ±21.0	286.9 ±25.9
	Method 3[c]		19.5 ±2.3	190.9 ±2.1	191.5 ±1.7	374.2 ±0.8	720.9 ±5.1	527.9 ±2.2

[a] the microwave-ICP method. Data reported are calculated from repeated tests conducted by ChemCentre. [b] the ashing-digestion-IC method.

[c] the evaporation-ashing-digestion-IC method with program 4.

bioslurry A, 5% biochar, bioslurry A, 10% biochar, and bioslurry A, 20% biochar: bioslurry fuels prepared from bio-oil A at biochar-loading levels of 5 wt%, 10 wt%, and 20 wt% respectively; bioslurry B, 10% biochar: bioslurry fuel prepared from bio-oil B at a biochar-loading level of 10 wt%.

Third, the concentrations of AAEM species in bioslurry fuels quantified by the ashing–digestion–IC method are generally lower than those from the microwave–ICP method. This is particularly the case for bioslurry fuels with high biochar-loading levels (e.g., 10 and 20 wt%). As aforementioned, the microwave–ICP method already underestimates the concentrations of AAEM species in biochar because of incomplete oxidation of biochar particles. The even lower concentrations of AAEM species in bioslurry fuels quantified by the ashing–digestion–IC method indicate that, during ashing, at least part of AAEM species in the bioslurry samples was lost. For example, in presence of biochar at high loading levels, some of biochar particles may have been carried out of the crucible because of intensive evaporation. Clearly, the temperature-time program designed for biomass and biochar is not applicable to bioslurry fuels. Therefore, a new development is required to modify the existing ashing–digestion–IC method for quantifying AAEM species in bioslurry fuels.

4.3 Design and Development of an Evaporation–Ashing–Digestion–IC Method

As discussed in Section 4.2, apart from accurate quantification of AAEM species in biochar, the current ashing–digestion–IC method is also applicable to bio-oil, indicating that evaporation of bio-oil vapors results in negligible loss of AAEM species. In other words, the evaporated bio-oil vapors are most likely free of AAEM species. However, the ashing–digestion–IC method substantially underestimates the contents of AAEM in bioslurry fuels, possibly as a result of the carry-over of biochar particles during ashing. In other words, when the temperature-time program that is designed for the ashing of biomass and/or biochar is applied to bioslurry, it appears that the rapid evaporation of bio-oil in bioslurry also may carry some of the biochar particles out of the ashing crucible, leading to the loss of AAEM species. Therefore, incorporating a suitable evaporation step into the current ashing program is the key to adapting the ashing–digestion–IC method to bioslurry. Such an evaporation step must progressively evaporate bio-oil vapors slowly in order to avoid the carry-over of

biochar particles. Therefore, a so-called "evaporation–ashing–digestion–IC" method is therefore developed, with the detailed design illustrated in Figure 4-2. Essentially, the new method consists of four steps, including (1) homogeneous sampling, (2) progressive evaporation followed by ashing, (3) acid digestion, and (4) quantification by IC. Whereas other steps are consistent with those of the ashing–digestion–IC method,[36,207-209] key innovation of the evaporation–ashing–digestion–IC method is the smart design of a suitable bio-oil evaporation step. The design of such a step must not only convert a bioslurry fuel into a residue (solid-like) via evaporation accompanied with carbonization, but also avoid the carry-over of biochar particles, so that the process must be slow (i.e. progressive). In this way, the solid-like residue after the progressive evaporation can then be subjected to the subsequent ashing that completely oxidizes and converts the solid-like residue into ash to achieve 100% retention of AAEM species.

The design of such a progressive evaporation step therefore must be based on the evaporation, pyrolysis and also combustion behavior of bio-oil. It is known that bio-oil is a complex mixture of water and various organic compounds plus a small amount of inorganic matter.[34,107] Previous TGA analysis suggests that, upon heating in air atmospheres, there are three distinct stages of bio-oil transformation, including evaporation of water and light volatile compounds, cracking of heavy compounds and formation of secondary char, and combustion of the secondary char.[226-228] It was reported that significant weight loss (over 70%) of bio-oil takes place at temperatures below 277 ^{o}C, where secondary char is formed.[226-232] Therefore, in this study, it is plausible to set the upper temperature of the progressive evaporation step to be 277 ^{o}C. To ensure the evaporation of bio-oil is indeed progressive and slow, it is also essential to design and deploy necessary temperature intervals according to boiling points of the major compounds present in bio-oil. Figure 4-3 presents boiling points of major bio-oil compounds based on data reported by Branca et al.[228] It can be seen that the major compounds in bio-oil can be fractioned into five groups in the temperature range

of room temperature to 277 ^{o}C according to their boiling points.[228] Correspondingly, the five segment temperatures (i.e. 87, 127, 177, 227, and 277 ^{o}C, respectively) are then chosen in the design of five temperature-time program for evaporation shown in Figure 4-4. These five programs are designed and evaluated to determine the optimum evaporation conditions that minimize biochar carry-over and consume less time. In Program 1, the bioslurry sample is directly heated from room temperature to 277 ^{o}C at a heating rate of 10 ^{o}C/min. The program is consistent with the ashing program of the ashing–digestion–IC method and used for benchmarking. Program 2 also employs direct heating but lowers the heating rate to 5 ^{o}C/min. Programs 3−5 apply the five segment temperatures identified in Figure 4-3 but employ different heating rate (1–5 ^{o}C/min) and holding time (10–30 mins) at each segment temperature. As the weight loss profile of bio-oil in air or inert atmosphere is similar at temperatures below 277 ^{o}C,[226,227] air is used during the whole process of progressive evaporation and subsequent combustion. During the experiment, around 0.5 g bio-oil or bioslurry is loaded in each Pt crucible, considering the crucible volume and space required for bio-oil swelling.[228]

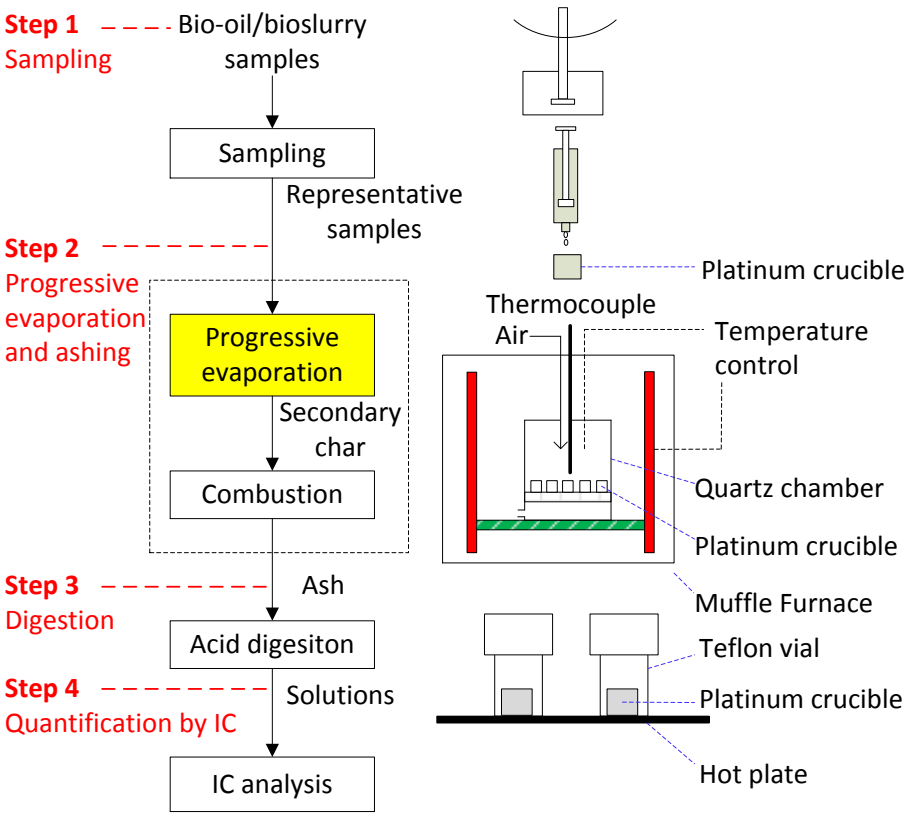

Figure 4-2 Schematic diagram of the evaporation-ashing-digestion-IC method for the quantification of AAEM species in bioslurry fuels

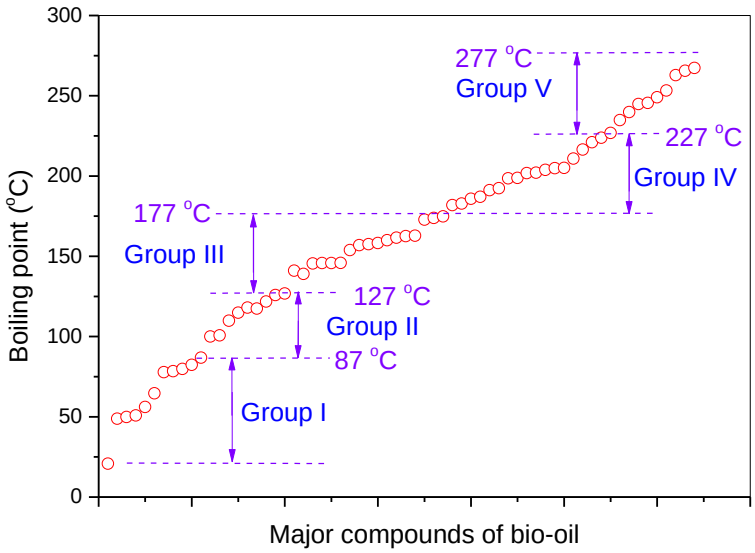

Figure 4-3 Boiling points of major compounds in bio-oil. Data are taken from Branca et al.[228]

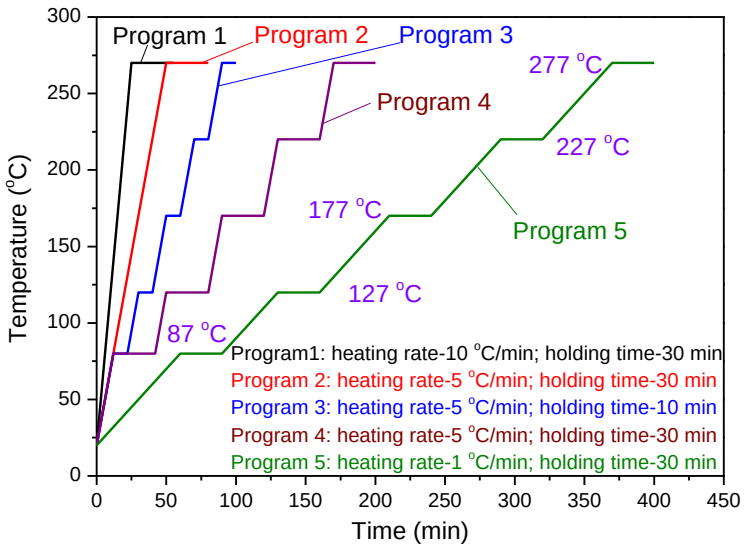

Figure 4-4 Design of five different progressive evaporation programs used in the evaporation-ashing-digestion-IC method

4.4 Application of the Evaporation-Ashing-Digestion-IC Methods in Quantification of AAEM Species in Bioslurry Fuels

The evaporation–ashing–digestion–IC method was then applied to quantify AAEM species in bioslurry samples, using the five evaporation programs. Similar analyses were also conducted for bio-oil samples. As shown in Figure 4-5, the concentrations of AAEM species in bio-oil are insensitive to the evaporation program used, further confirming that the loss of AAEM species during bio-oil evaporation is negligible. However, the data in Figure 4-6 show that the concentrations of AAEM species in bioslurry samples are strongly dependent on the evaporation program used. Therefore, this clearly suggests the critical importance of both heating rate and progressive temperature control during bioslurry evaporation.

Program 1 substantially underestimates concentrations of AAEM species for all of the bioslurry fuels studied, apparently because of both the direct heating from room temperature to 277 °C without holding at key segment temperatures and also the high heating rate employed (i.e. 10 °C/min). It seems that a large amount of bio-oil

compounds can be simultaneously evaporated under the conditions, leading to the carry-over of biochar particles and consequent underestimation of AAEM species in bioslurry. Indeed, when the heating rate is reduced from 10 to 5 ^{o}C/min, Program 2 appears to be capable of minimizing such carry-over and becoming sufficient for the quantification of AAEM species in all bioslurry fuels other than bioslurry A with 20 wt% biochar loading.

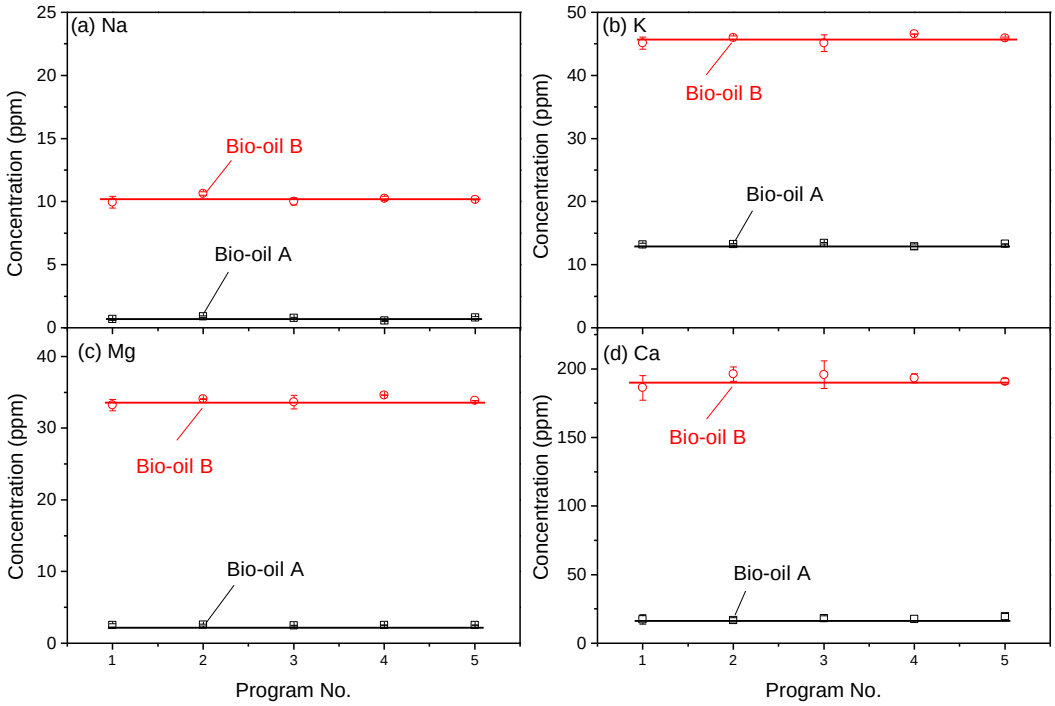

Figure 4-5 Concentration of (a) Na, (b) K, (c) Mg, and (d) Ca in the bio-oil quantified using the evaporation-ashing-digestion-IC method with five different evaporation programs

However, in addition to a slow heating rate (e.g., 5 ^{o}C/min), progressive temperature control via holding at key segment temperatures during the process of evaporation is also required for quantification of AAEM species in bioslurry with high biochar-loading levels (i.e. bioslurry A with 20 wt% biochar, see panels i–l of Figure 4-6). For bioslurry A with 20 wt% biochar, the AAEM concentrations quantified by Program 2 are considerably lower than those quantified by Programs 3−5. It should be noted that the only difference between Program 2 and Program 3 is that the latter

employs progressive temperature control (i.e. holding 10 min at each segment temperature, see Figure 4-4). The substantial differences in the concentrations of AAEM species between Programs 2 and 3 clearly indicate that both slow heating (5 ^{o}C/min or below) and holding at key segment temperatures (10 mins or longer) must be adapted in the design of the temperature-time program for effective progressive evaporation. Such temperature-time program is essential to enabling slow evaporation and carbonization of bioslurry without the carry-over effect. Clearly, the results also imply that increasing biochar-loading level may intensify its carry-over during bioslurry evaporation, possibly because of an increase in biochar particle population in bioslurry and also a decrease in bioslurry mobility.[27]

A further decrease in heating rate from 5 to 1 ^{o}C/min and an increase of holding time from 10 to 30 min appear to be not necessary because there are little changes in the concentrations of AAEM species quantified by Programs 3–5. Therefore, considering the quality of results and the time required, program 4 is recommended as the optimum progressive evaporation program for all of the bioslurry fuels studied under the experimental conditions. The concentrations of AAEM species obtained from program 4 are then used as representative values quantified by the evaporation–ashing–digestion–IC method as presented in Table 4-2. Figure 4-7 further shows that the measured concentrations of AAEM species in bioslurry fuels are in good agreement with the estimated values that are calculated based on the AAEM concentrations in bio-oil and biochar, considering their mass fractions in the bioslurry samples. Therefore, direct quantification of AAEM species in bioslurry fuels eases analytical work in bioslurry central unitization plants, because separate analysis of bio-oil and biochar is not required. In addition, the evaporation–ashing–digestion–IC method (Program 4) can also be used for quanitfying AAEM species in either biochar, bio-oil or bioslurry fuels.

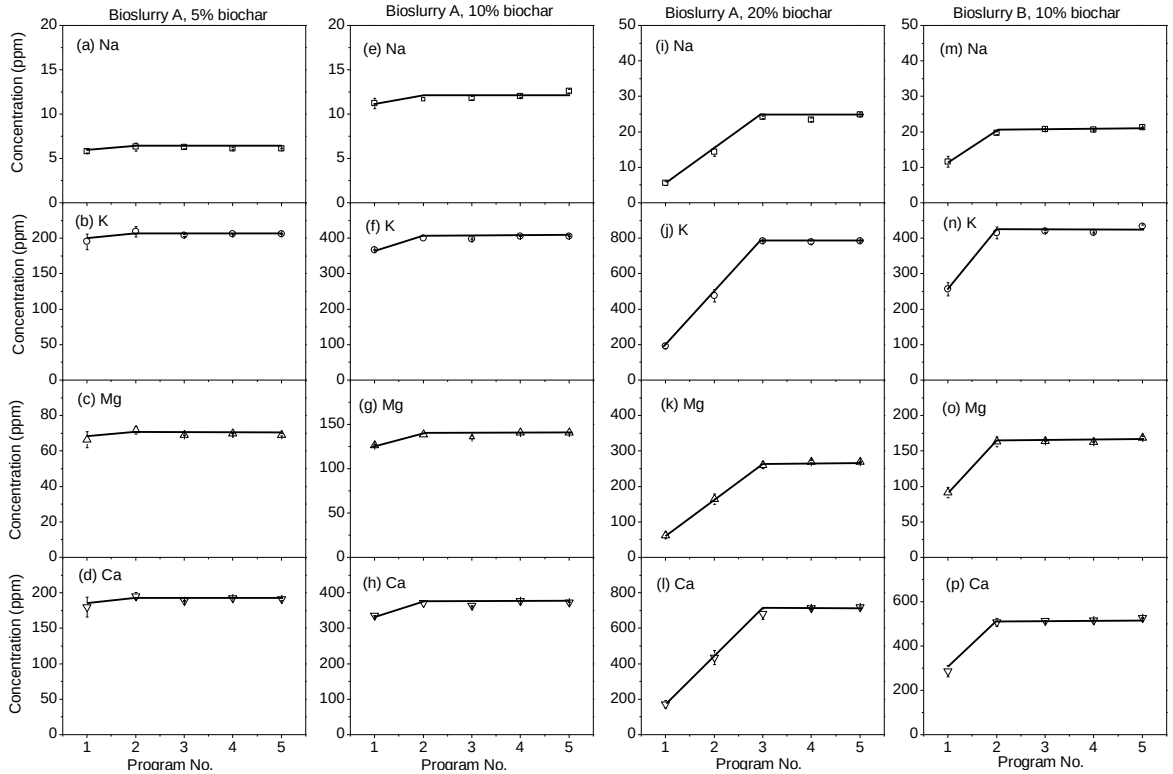

Figure 4-6 Concentrations of Na, K, Mg, and Ca in the bioslurry fuels quantified by the evaporation-ashing-digestion-IC method with 5 different evaporation programs for bioslurry prepared from bio-oil A with biochar loading of 5 wt% (panels a-d), 10 wt% (panels e-h), and 20 wt% (panel i-l) and bioslurry prepared from bio-oil B with biochar loading of 10 wt% (panels m-p)

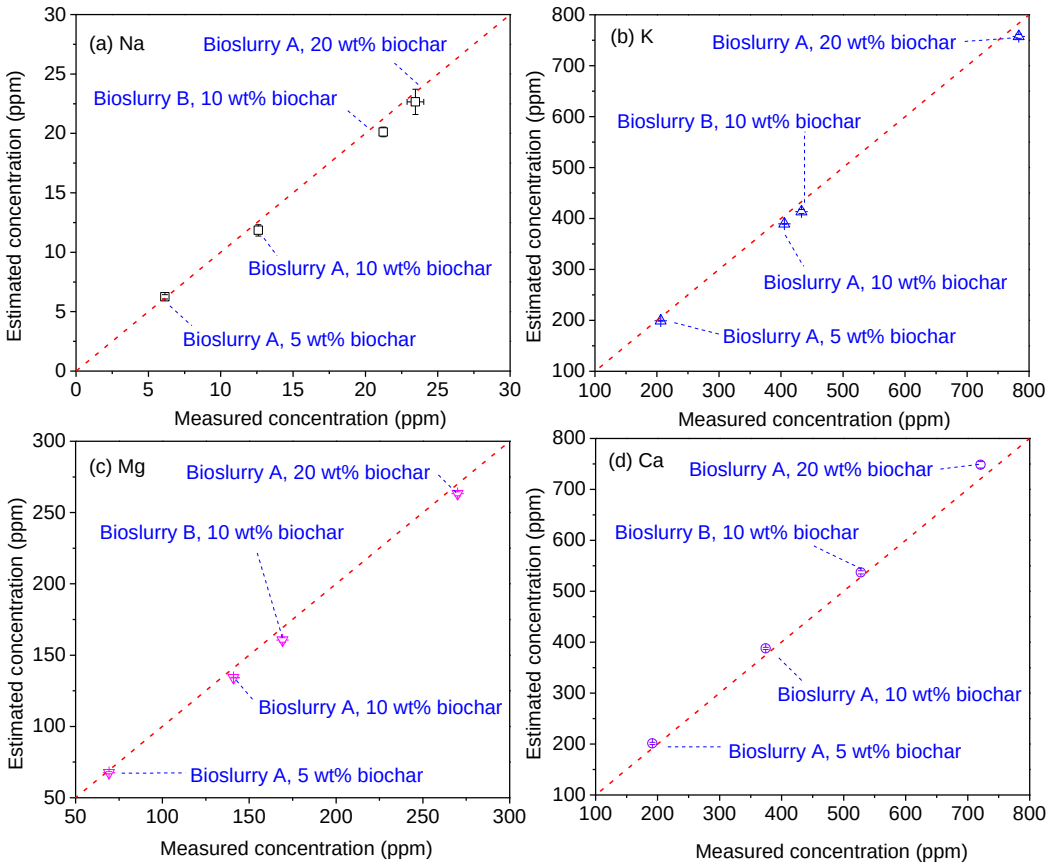

Figure 4-7 Comparison of measured and estimated values of AAEM concentration in bioslurry fuels quantified by the evaporation-ashing-digestion-IC method with program 4

4.5 Further Discussion

The evaporation–ashing–digestion–IC method offers at least three advantages. First, the method achieves effective ashing while also retaining the AAEM species in the ash. This is clearly shown in Table 4-2, where the concentrations of AAEM species quantified by the evaporation–ashing–digestion–IC method are higher than those obtained from the microwave digestion–ICP method, especially for bioslurry with high biochar-loading level (e.g., 20 wt%). This also points to the issue of incomplete oxidation of biochar in bioslurry samples by microwave digestion (see Figure 4-1).

Second, the relative standard errors of the evaporation–ashing–digestion–IC method

are generally within ±3%, which is much smaller than those (±13%) of the microwave–ICP method. The reason is that, to prevent explosion, the sample amount is limited to 0.2 g or less during microwave digestion (see Section 3.4.2). This is considerably smaller than that of the evaporation–ashing–digestion–IC method (~0.5 g, see Section 4.3).

Third, the limitation of quantification (LOQ) of the evaporation–ashing–digestion–IC method is also low (0.4−3.0 ppm) depending upon the AAEM species. LOQ is calculated as the instrument detection limit times the final solution volume divided by the sample size, as reported in the literature.[233] The calculated LOQ for AAEM species using the evaporation–ashing–digestion–IC and microwave-ICP methods are presented in Table 4-3, because both methods are suitable for bio-oil analysis. The evaporation–ashing–digestion–IC method yields a lower LOQ for all AAEM species. In comparison to the results from the microwave–ICP method, the lower LOQ of the evaporation–ashing–digestion–IC method can be mainly attributed to the larger sample size and smaller acid volume used in the method. As aforementioned, the sample size used in the evaporation–ashing–digestion–IC method is twice as that used in the microwave–ICP method. Therefore, a lower LOQ of the evaporation–ashing–digestion–IC method can be expected. In addition, the microwave–ICP method requires considerably more acid (~20 mL) than the evaporation–ashing–digestion–IC method (~4 mL), which contributes to a higher background because of the impurities inevitably presented in the acids used.

Table 4-3 Limitations of quantification (LOQ) for the microwave-ICP and evaporation–ashing–digestion–IC methods

Method	LOQ (ppm)			
	Na	K	Mg	Ca
microwave-ICP method	10	1	2	20
evaporation–ashing–digestion–IC method	0.7	0.4	0.6	3.0

4.6 Conclusions

This study develops a new evaporation–ashing–digestion–IC method that is capable of quantifying AAEM species in bioslurry fuels. The method consists of four steps: evaporation converting biolsurry into a solid-like residue, ashing converting the residue into ash, acid digestion dissolving the ash into a solution and IC analysis quantifying the AAEM species in the solution. It is developed from the conventional ashing–digestion–IC method that is designed for quantifying AAEM species in solid fuels but underestimates these values in bioslurry fuels because of the carry-over of biochar particles during ashing. The new method includes an evaporation step that consists of multiple segments (slow heating and holding) at temperatures corresponding to the boiling points of the major compounds in bio-oil for avoiding the carry-over of biochar particles. The method can accurately determine the concentrations of AAEM species in bioslurry fuels with various biochar loading levels (5–20 wt%). The relative standard errors are small (within ±3%) and the limitations of quantification are low (0.4−3.0 ppm). In comparison to the conventional methods based on microwave digestion, the new method also overcomes the biochar incomplete oxidation issue that leads to considerable underestimation of the concentrations of AAEM species.

CHAPTER 5 FUEL PROPERTIES EVOLUTION AND AGEING DURING BIOSLURRY STORAGE

5.1 Introduction

A series of recent studies on bioslurry fuel by Wu et al[24,27,28,182] have shown that a bioslurry supply chain is economically viable, the energy and carbon footprints of bioslurry fuel from mallee biomass are small, and bioslurry fuels prepared from fresh bio-oil or bio-oil rich fraction have desired fuel and rheological properties for stationary applications. However, bio-oil, as one of the two major components used for preparing bioslurry fuels, is well known for its ageing during storage at room temperature or short time at elevated temperature.[29-33] Bio-oil ageing leads to changes in viscosity, water content, homogeneity, and acidity of bio-oil which are important characteristics to be considered for fuel application.[18,22] It is known that bio-oil ageing is closely associated with underlying chemical reactions occurred in bio-oil and also can be exacerbated at elevated temperature and potentially catalyzed by inherent catalytic species [particularly alkali or alkaline earth metallic (AAEM) species].[34,35] However, little work has been performed thus far on the ageing, hence the changes in properties of bioslurry fuels during storage. Particularly, it is largely unknown how bioslurry fuel stability and rheological properties will evolve with time during storage. It is also unclear what roles the large quantity of biochar presented in a bioslurry can play in the ageing and chemical stability of the bioslurry fuel.

Therefore, this chapter focuses on fuel properties evolution and the ageing of bioslurry fuels during storage. The ageing experiments of bioslurry fuels at room temperature were carried out, considering a series of biochar loading levels. Sampling was periodically performed for the bioslurry samples in the process of ageing at various lengths of periods up to 29 days. The collected bioslurry samples were separated into

solid and liquid samples which were subsequently subjected to an array of analyses, including those for rheology, viscosity, water content, total acid number (TAN) and concentrations of AAEM species. Table 5-1 presents the properties of filtered bio-oil A, filtered bio-oil B and the biochar samples used in this chapter.

Table 5-1 Properties of the bio-oil (filtered) and biochar samples used in Chapter 5

Samples	Bio-oil A	Bio-oil B	Biochar
Proximate analysis			
Water content (wt%, ar[a])	24.4	28.3	1.6
Ash (wt%, db[b])	nd[c]	nd[c]	5.7
Volatile matter (wt%, db[b])	nd[c]	nd[c]	22.0
Fixed carbon (wt%, db[b])	nd[c]	nd[c]	72.3
Elemetal analysis (wt%)			
C[a,d]	42.76	40.22	79.51
H[a,d]	7.26	7.51	2.68
N[a,d]	0.29	0.31	0.14
O[e]	49.69	51.96	17.67
Na[a,b]	0.0001	0.0010	0.0101
K[a,b]	0.0014	0.0047	0.3771
Mg[a,b]	0.0002	0.0035	0.1364
Ca[a,b]	0.0014	0.0179	0.3504
Viscosity (40 °C, mPa s)	54.3	28.8	
TAN[f] (mg NaOH/g bio-oil)	49.1	46.3	

[a] as received basis for bio-oil. [b] dry basis for biochar. [c] not determined. [d] dry and ash free basis for biochar. [e] by difference. [f] total acid number.

5.2 Evolution of Rheological Characteristics of Bio-oil in Bioslurry during Storage

Figure 5-1 presents the experimental data on the evolution of rheological characteristics of bio-oil in bioslurry during storage. The data in Figure 5-1 show that the shear stress and viscosity changes as a function of shear rate. All the bio-oil samples exhibit slight shear-thinning characteristics at a shear rate less than 50 s^{-1} but overall the fluid behaviours are predominantly Newtonian. This is consistent with the findings reported previously.[27,28] The shear thinning behaviour below 50 s^{-1} may be

attributed to the break-down of gel structure of the bio-oil because waxy materials are known to present in softwood pyrolysis liquid.[111] Although a thixotropic characteristic was expected from such material as the gel structure being destructed and reorganized, the hysteresis loop of all of the bio-oil samples are generally insignificant, as indicated in Figure 5-2. The slightly higher shear stress along the downward ramp than along the upward ramp may be due to slight evaporation of some light molecules at 40 °C during analysis. The viscosity of bio-oil samples as function of the storage time is presented in Figure 5-3. The change in viscosity of the blank bio-oil samples is negligible over the storage of 29 days. This is likely due to the long term (over 6 months) preservation of the bio-oil samples before use. A previous study[32] has shown that the changes in the properties of a fast pyrolysis bio-oil from forestry residue were significant in the first month after production and the change rate diminished gradually and levelled off after 6 months. In another study,[91] the variation in viscosity retarded after 65 days for a bio-oil produced from a softwood bark.

However, there are some interesting observations from the data presented in Figure 5-1 and Figure 5-3. There are significant decreases in the viscosity of the bio-oil samples separated from the bioslurry samples after various periods of ageing. After 29 days, the viscosity decreases by approximately 36 and 27% for bio-oil A and B respectively. This clearly demonstrates the significant effect of biochar particles on bioslurry ageing during storage. In the literature, it was generally considered that the inherent soot-like particles present in bio-oil, as inevitable results of bio-oil condensation and collection from the pyrolysis reactor systems, increase bio-oil viscosity during ageing.[33,35,234] However, the findings in this study (as shown in Figure 5-1 and Figure 5-3) clearly suggest that the biochar particles mixed into bio-oil for producing bioslurry fuels have an opposite effect on the rheology and viscosity of the bio-oil phase during bioslurry storage. Therefore, efforts were then taken to carry out further work for understanding this interesting observation, as reported in subsequent sections.

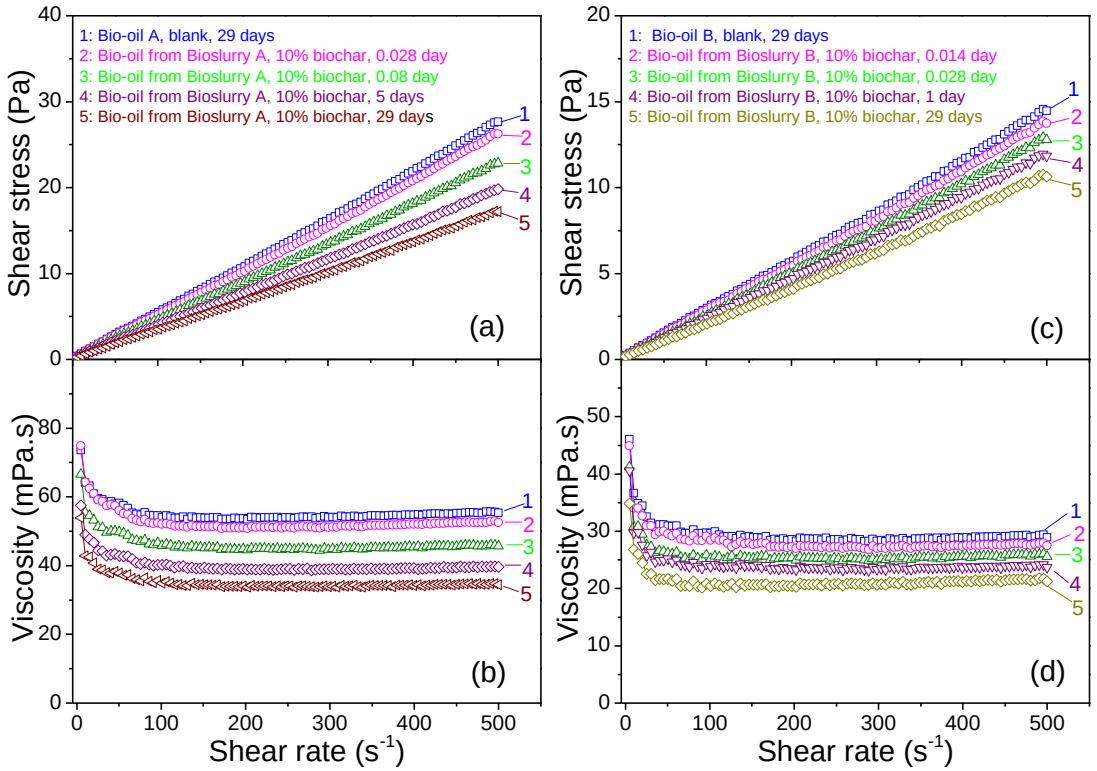

Figure 5-1 Shear stress and apparent viscosity of bio-oil samples as a function of shear rate. Bioslurry A and Bioslurry B, both of which have a 10 wt% biochar, were prepared from bio-oil A and bio-oil B, respectively. The data for the blank bio-oil samples are presented in the same panel with the bio-oil separated from bioslurry samples (panel a and b for bio-oil A; panel c and d for bio-oil B). Only the bio-oil blanks stored for 29 days are presented here

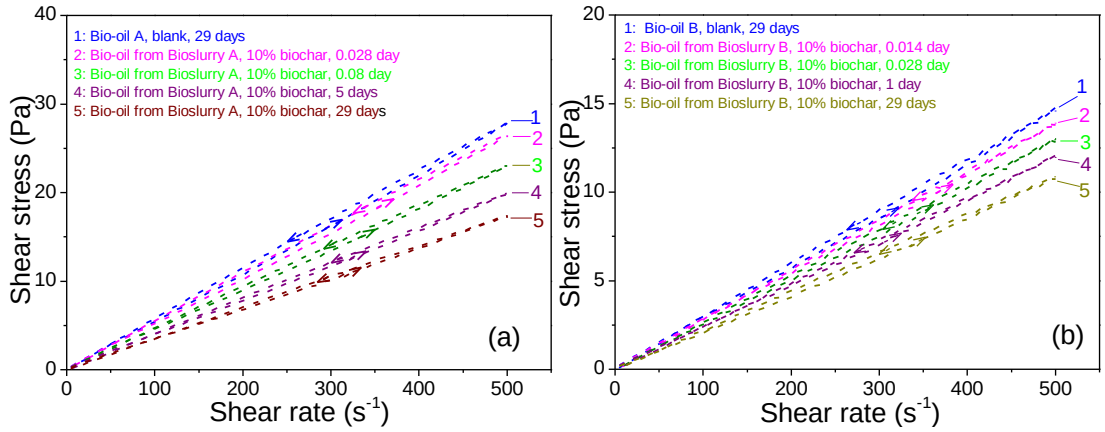

Figure 5-2 Thixotropic behaviour of bio-oil samples. Bioslurry A and Bioslurry B, both of which have a 10 wt% biochar, were prepared from bio-oil A and bio-oil B, respectively. The data for blank bio-oil samples are presented in the same panel with the bio-oil phases separated from bioslurry samples (panel a for bio-oil A; panel b for bio-oil B). Only the bio-oil blanks stored for 29 days are presented here

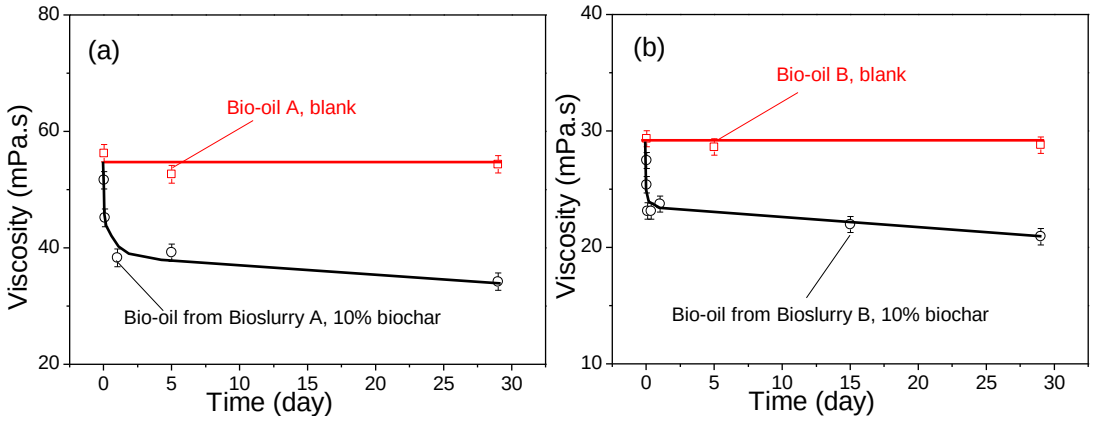

Figure 5-3 Evolution of viscosity of bio-oil during bioslurry storage. Bioslurry A and Bioslurry B, both of which have a 10 wt% biochar, were prepared from bio-oil A and bio-oil B, respectively. The data for the blank bio-oil samples are presented in the same panel with the bio-oil separated from bioslurry samples (panel a for bio-oil A; panel b for bio-oil B)

5.3 Evolution of Water Content and TAN of Bio-oil in Bioslurry during Storage

Figure 5-4 presents the data on the evolution of the water content of both the blank bio-oil and the bio-oil phase in bioslurry as a function of the storage time. There is little change in the water content of the blank bio-oil sample during the whole period of storage up to 29 days, consistent with the results reported in the previous section. However, the water content of the bio-oil phase in bioslurry exhibits a rapid increase within the first 24 hours, and such an increase levels off with further storage. After 29 days of storage, the increases in the water content of the bio-oil phase in bioslurry prepared from bio-oil A and bio-oil B with 10% biochar loading are approximately 2.8 and 2.3%, respectively. It is known that the viscosity of bio-oil strongly depends on the water content of bio-oil, and an increasing water content leads to a decrease in the viscosity of bio-oil.[35,235] Therefore, the data on the increment in the water content of bio-oil phase in bioslurry during storage are consistent with (and at least partially explains) the reduction in the viscosity of the bio-oil phase in bioslurry (see Figure 5-1and Figure 5-3).

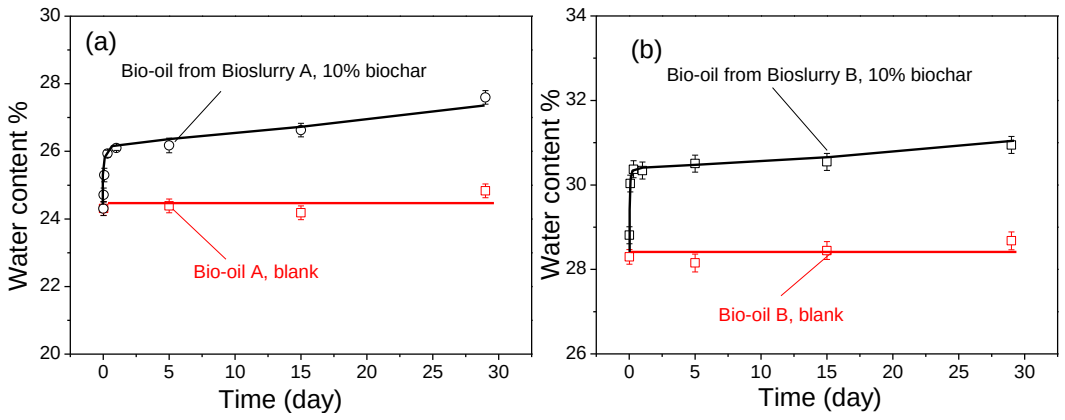

Figure 5-4 Evolution of water content of bio-oil during bioslurry storage. Bioslurry A and Bioslurry B, both of which have 10 wt% biochar, were prepared from bio-oil A and bio-oil B, respectively. The data for the blank bio-oil samples are presented in the same panel with the bio-oil separated from bioslurry samples (panel a for bio-oil A; panel b for bio-oil B)

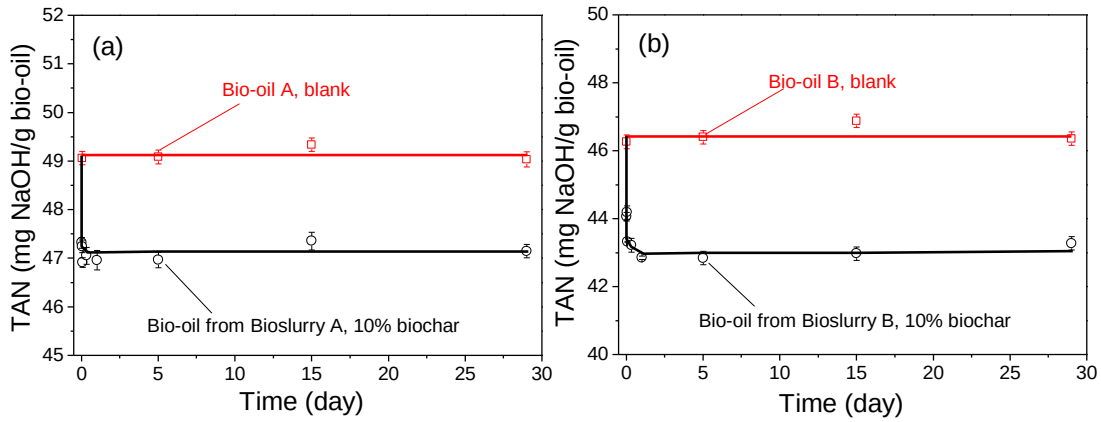

Figure 5-5 Evolution of TAN of bio-oil during bioslurry storage. Bioslurry A and Bioslurry B, both of which have a 10 wt% biochar, were prepared from bio-oil A and bio-oil B, respectively. The data for the blank bio-oil samples are presented in the same panel with the bio-oil separated from bioslurry samples (panel a for bio-oil A; panel b for bio-oil B)

Figure 5-5 further plots the changes in TAN of the bio-oil samples as function of the storage time. The TAN of the blank bio-oil samples remain unchanged, attributed to similar reasons given in the previous section for little change in the viscosity of blank bio-oils. However, for the bio-oil samples separated from the bioslurries after various ageing period, the values of TAN rapidly decrease within the first 24 hours after biochar particles suspended into bio-oil and level off with further storage. It is also noted that, while the initial TAN of the blank bio-oil A is higher than that of the blank bio-oil B (see Table 5-1), the reduction in the TAN of the bio-oil A separated from bioslurry fuels during storage is contrarily smaller than that of the bio-oil B. The reductions in the TAN are approximately 4 and 7% for bio-oil A and bio-oil B, respectively, suggesting the difference in the reactivity of the acid compounds in these two bio-oils.

When the data in Figure 5-1–Figure 5-5 are taken together, the results reported in this study demonstrate that suspending biochar into bio-oil for producing bioslurry fuels

leads to important changes in the properties of bio-oil phase of bioslurry fuels during storage. There are several mechanisms possibly responsible for the observed ageing behaviour of bioslurry fuels. First, it is well-known that bio-oil is a complex mixture with hundreds of organic compounds including acids, alcohols, aldehydes, ketones, furans, esters, phenols, sugars and compounds with multiple functional groups.[34] The reactions among these chemicals can occur during bio-oil storage with or without a catalyst, with possible reactions responsible for water increase including esterification, acetalization and polycondensation reactions.[20,31,34] Acetalization and polycondensation reactions are known to be catalysed by salts (chlorides, sulphate, phosphate etc.), especially salts of divalent metals such as calcium and magnesium.[34,236] Biochar contains abundant inherent inorganic species (see Table 5-1), which can potentially act as such catalysts for bioslurry ageing during storage. Second, esterification of acid and alcohol or olefin compounds is a well-recognized reaction responsible for acidity decrease and water increase during bio-oil ageing; however, such a reaction is very slow at room temperature without catalysts, and catalysts for esterification are usually acidic.[34,237,238] Therefore, there is the possibility that acidic functional groups presented on the surface of biochar[239,240] can catalyse this reaction and, hence, promote bioslurry ageing during storage. Third, biochar also contains basic functional groups on the surface and, overall, is generally alkaline, with inherent inorganic compounds also contributing to biochar alkalinity.[241,242] The pH of the biochar used in this study is 8.4, measured by suspending char in water (1:20 of biochar to water based on weight). Therefore, the acidic bio-oil can react with some basic functional groups (e.g., ketones, pyrones and chromens) on biochar surface[240] or with inorganic species in biochar,[242] leading to a reduction in TAN and an increase in water content of the bio-oil phase in bioslurry during storage. A reduction in TAN is the direct result of the consumption of H^+ in the bio-oil phase of bioslurry during storage. On the basis of the data in Figure 5-4 and Figure 5-5, even assuming all the consumption of H^+ only leads to the formation of water, which is unlikely considering

part of H^+ may participate in other reactions, such as ion exchange, the total H^+ consumption (estimated based on the reduction in TAN in Figure 5-5) can only account for a small proportion (<5%) of the observed increase in water content (see Figure 5-4). Therefore, acetalization and/or polycondensation among organic compounds in bio-oil appear to be the dominant mechanisms for the increase in the water content of the bio-oil phase during bioslurry storage.

5.4 Redistribution of AAEM Species between Biochar and Bio-oil during Bioslurry Storage

Figure 5-6 presents the data on the leaching of Na, K, Mg and Ca out of the biochar in the bioslurry samples over the period of 29 days for bioslurry storage. The data show that substantial amounts of AAEM species can be leached from the biochar during bioslurry storage. This is expected because acid washing is known to remove some of the AAEM species in biochar[36] and the bio-oils are acidic (see Figure 5-5). Figure 5-6 also indicates that higher quantities of the AAEM species can be leached from the biochar in bioslurry prepared from bio-oil B compared to those from bio-oil A, reflecting the different actions resulting for the difference in both the acid strength of the organic acids and the contents of water in these two bio-oils.

Further efforts were taken to investigate the evolution of the concentrations of AAEM species of bio-oil as a function of the storage time. The data in Figure 5-7 indicate that after 29 days of bioslurry storage, the leaching of Na, Mg and Ca from the biochar in the bioslurry samples approaches equilibrium while the leaching of K still proceeds at a very slow rate. A plot of $\ln C/C_0$ versus time (see the details of the method given elsewhere[243]) can provide useful insights into the leaching kinetics and mechanisms. As shown in Figure 5-8, the leaching of AAEM species from the biochar present in the bioslurry samples exhibits two leaching steps, including a rapid leaching step in first 24 hours and a subsequent slow leaching step during the remaining period of storage.

The first rapid leaching step can be attributed to the dissolution of some inorganic components (e.g., salts), which are soluble in the water or organic solvents present in the bio-oil phase of the bioslurry samples. The second slow leaching step is most likely due to the leaching of organically bound AAEM species via ion exchange with organic acid presented in the bio-oil phase of the bioslurry samples. It is also noted that the leaching rate of K appears to be slower than those of Na, Mg and Ca. While the exact reasons are unknown, one of the possibilities is that K may be present in the biochar in the form of intercalation in carbon matrix, thus retarding the leaching rate of K.[244-246]

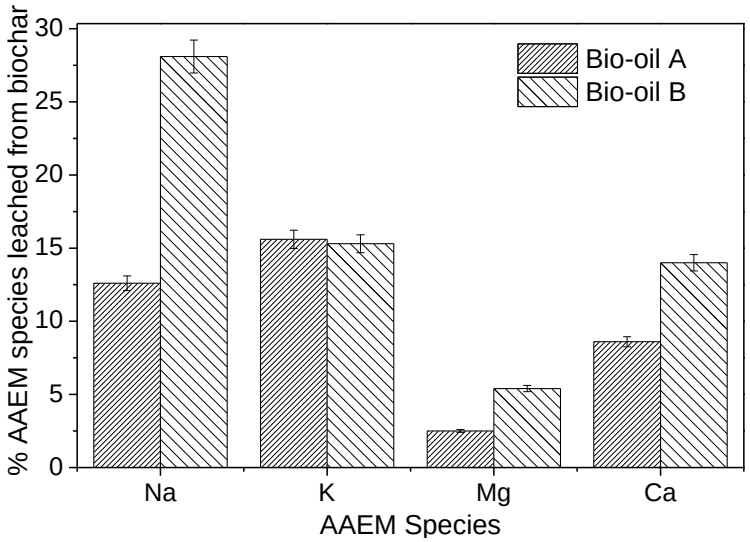

Figure 5-6 Percentage of AAEM species leached from biochar after the storage of bioslurry samples for 29 days. Bio-oil A and Bio-oil B in the legends indicate the data for bioslurry A and bioslurry B samples, both of which have a biochar loading level of 10% (based on weight) and were prepared from bio-oil A and bio-oil B, respectively

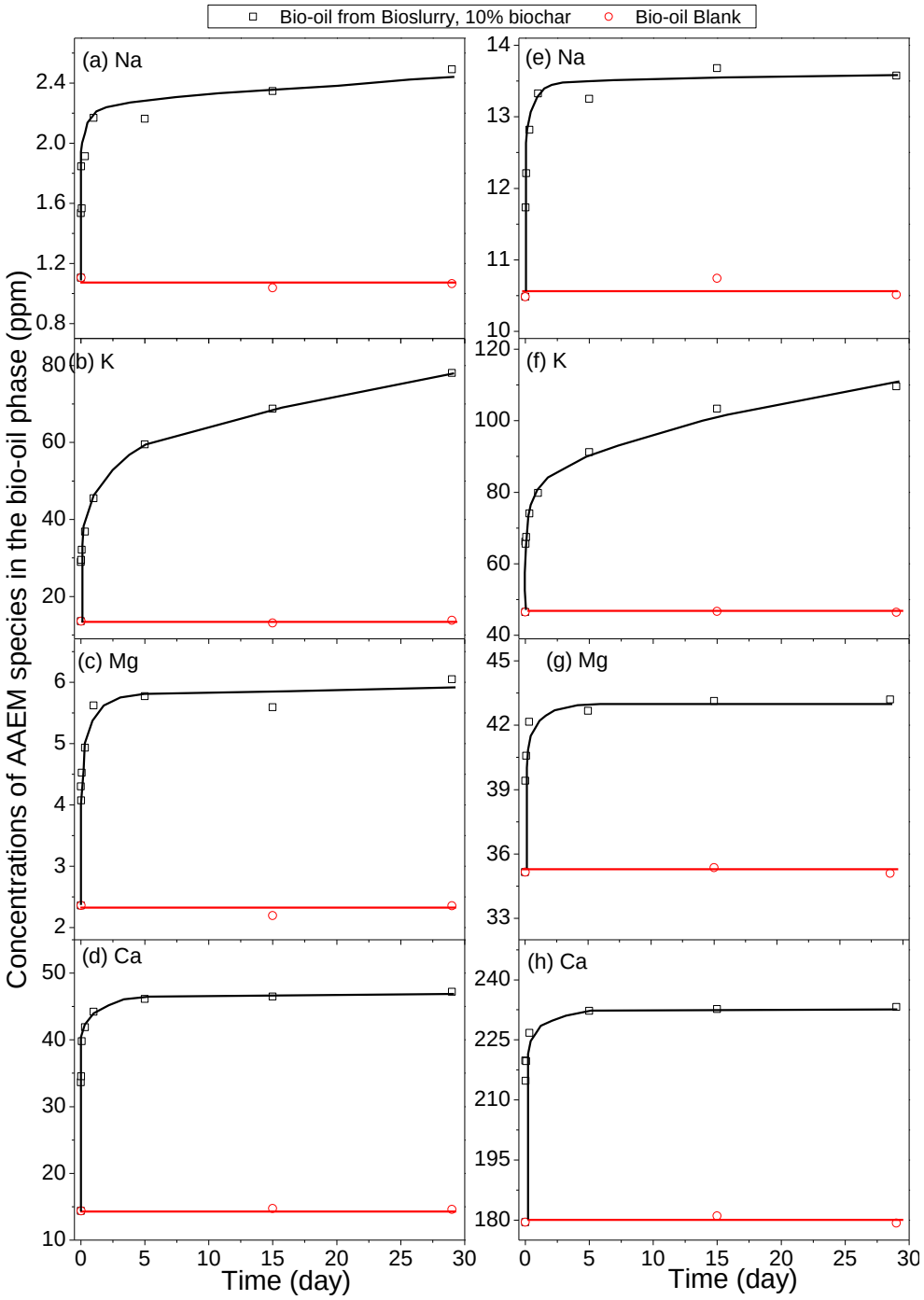

Figure 5-7 Evolution of the concentrations of AAEM species in the bio-oil phase during bioslurry storage. Bioslurry A and bioslurry B, both of which have 10% biochar (based on weight), were prepared from bio-oil A and bio-oil B respectively. The data for the blank bio-oil samples are presented in the same panel with those for the bio-oil phase separated from bioslurry fuels. Panels a–d are for Na, K, Mg and Ca in bio-oil A and panels e–h are for Na, K, Mg and Ca in bio-oil B, respectively

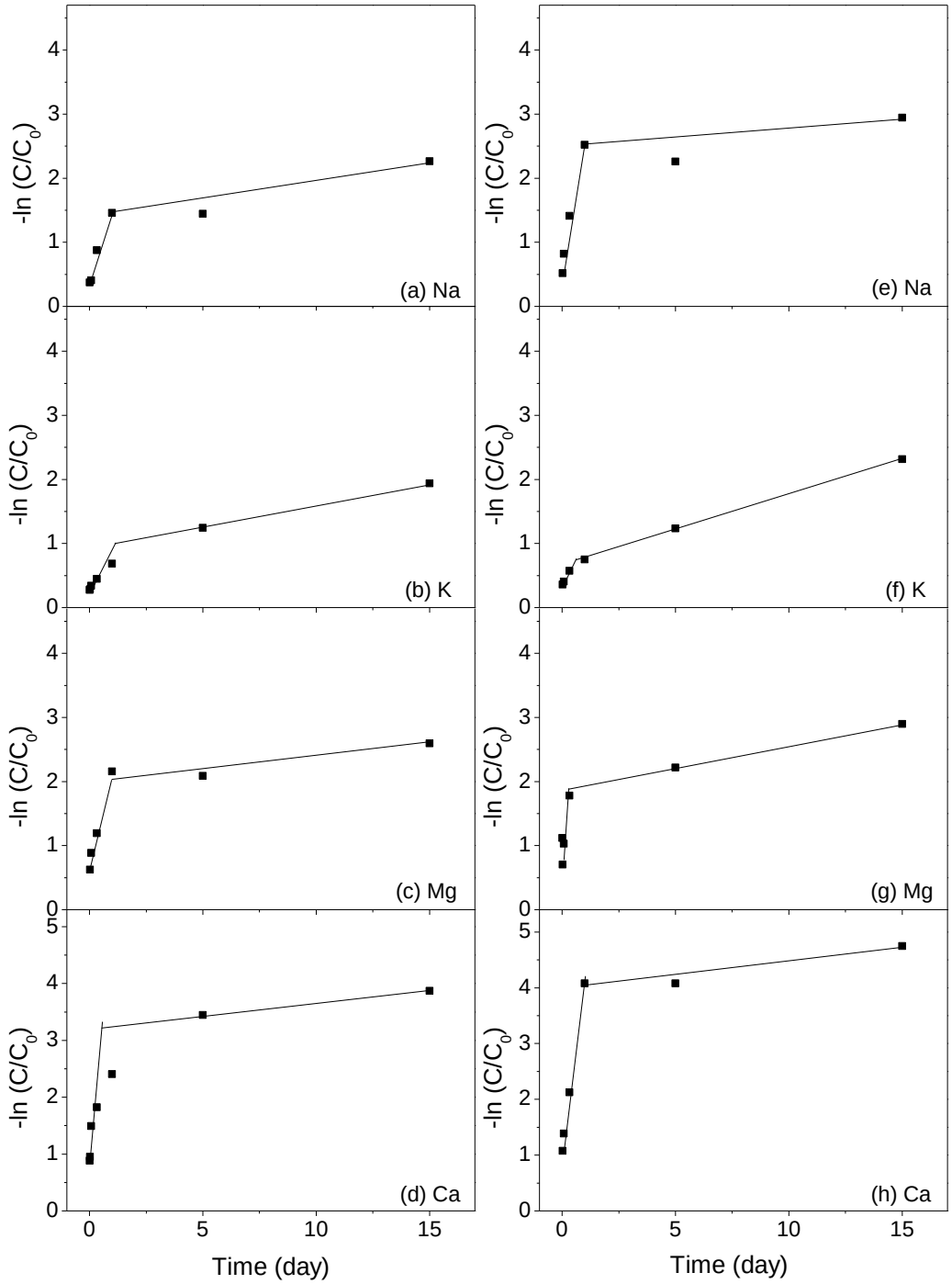

Figure 5-8 Plot of -ln(C/C_0) as a function of the storage time, with panels a–d for Na, K, Mg and Ca in the bio-oil separated from bioslurry A with 10 wt% biochar; and panels e–h for Na, K, Mg and Ca in the bio-oil separated from bioslurry B with 10 wt% biochar. Bioslurry A and bioslurry B were prepared from bio-oil A and bio-oil B, respectively

Some calculations were then carried out to estimate the consumption of organic acids in the bio-oil phase and the quantity of AAEM species (Na + K + 2Mg + 2Ca) leached from biochar. Even with a conservative assumption that all of the AAEM species are leached via ion exchange, it is interesting to note that the total quantity of acid needed for ion exchange contributes merely up to ~7% of the total reduction in the TAN of the bio-oil phase during bioslurry storage. Because not all AAEM species leached from the biochar is via ion exchange, the actual amount of acid took part in the leaching process is therefore small. Therefore, the data further confirm that the reduction in the TAN of the bio-oil phase is dominantly due to reactions of acidic bio-oil with basic functional groups on biochar surface or catalysed esterification within bio-oil, as discussed in the previous section. Although the fact that the sharp increase in the concentrations of AAEM species in the bio-oils in the first day coincides with a significant decline in the TAN of the bio-oils in the first day may suggest leaching of AAEM species causing significant reduction in TAN of bio-oil, this simple calculation suggests otherwise.

5.5 Further Discussion and Practical Implications

Figure 5-9 shows that an increase in the biochar loading level results in an increase in the quantity of AAEM species leached from the biochar into the bio-oil phase during bioslurry storage. The figure shows that the leaching of AAEM species correlates well with the biochar/bio-oil ratio in bioslurry. Figure 5-10 presents the distribution of AAEM species between the biochar and the bio-oil phase in the bioslurry samples at 0 and 29 days of storage. The results show that substantial quantities of AAEM species can be leached from the biochar into the bio-oil phase and such leaching increases with increasing biochar loading in bioslurry. Therefore, it is likely that solubility of AAEM species in the bio-oil phase is not the limiting factor for the leaching of AAEM species from the biochar during bioslurry storage. Additionally, while substantial quantities of AAEM species can be leached from the biochar into the bio-oil phase, the majority of

AAEM species in the bioslurry is still distributed in the biochar.

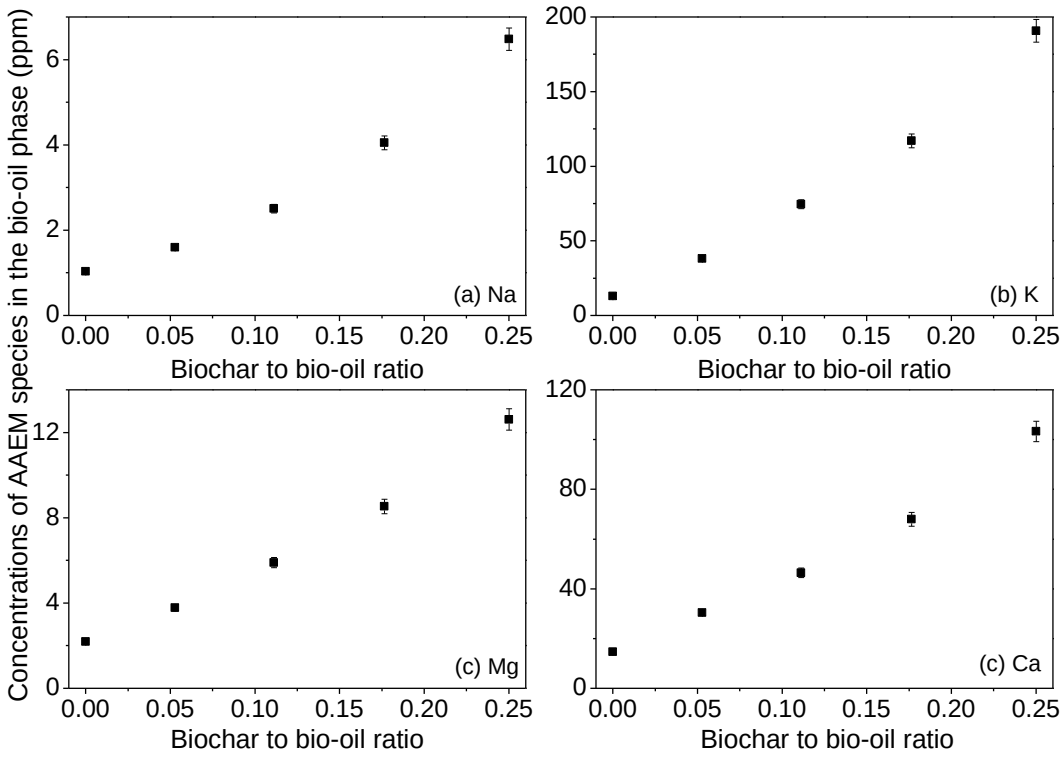

Figure 5-9 Concentrations of AAEM species in the bio-oil phase as a function of biochar to bio-oil ratio (biochar/bio-oil, based on weight) in bioslurry prepared from bio-oil A. A biochar to bio-oil ratio of zero represents the blank bio-oil sample

An increase in the amount of the biochar added into the bio-oil during bioslurry preparation results in a decrease in the TAN value and an increase in the water content of the bio-oil phase after 29 days of bioslurry storage. As shown in Figure 5-11(b), both the TAN and the water content of the bio-oil phase correlates almost linearly with the biochar/bio-oil ratio. It should be noted that the increase of water content normalized to initial water content in blank bio-oil (~13%) is considerably higher than the decrease of TAN normalized to initial TAN in blank bio-oil (~5%). This indicates that the loading of biochar into bioslurry fuels has a more profound effect on the water content than the TAN of bioslurry fuels. As discussed previously, acetalization and/or polycondensation are the dominant mechanisms responsible for the increase in the

water content and these reactions can be catalysed by inorganic species present in the bioslurry fuels. Therefore, it appears that an increase in biochar loading leads to the increased availability of such catalysts for the acetalization and/or polycondensation reactions during bioslurry ageing. This is supported by the data in Figure 5-11(a), which clearly shows that the viscosity of the bio-oil phase in bioslurry decreases with increasing biochar loading. In addition, the viscosity of the bio-oil versus the ratio of biochar to bio-oil in bioslurry follows a power-law correlation. A similar correlation was also reported between the viscosity and the water content for bio-oils.[235]

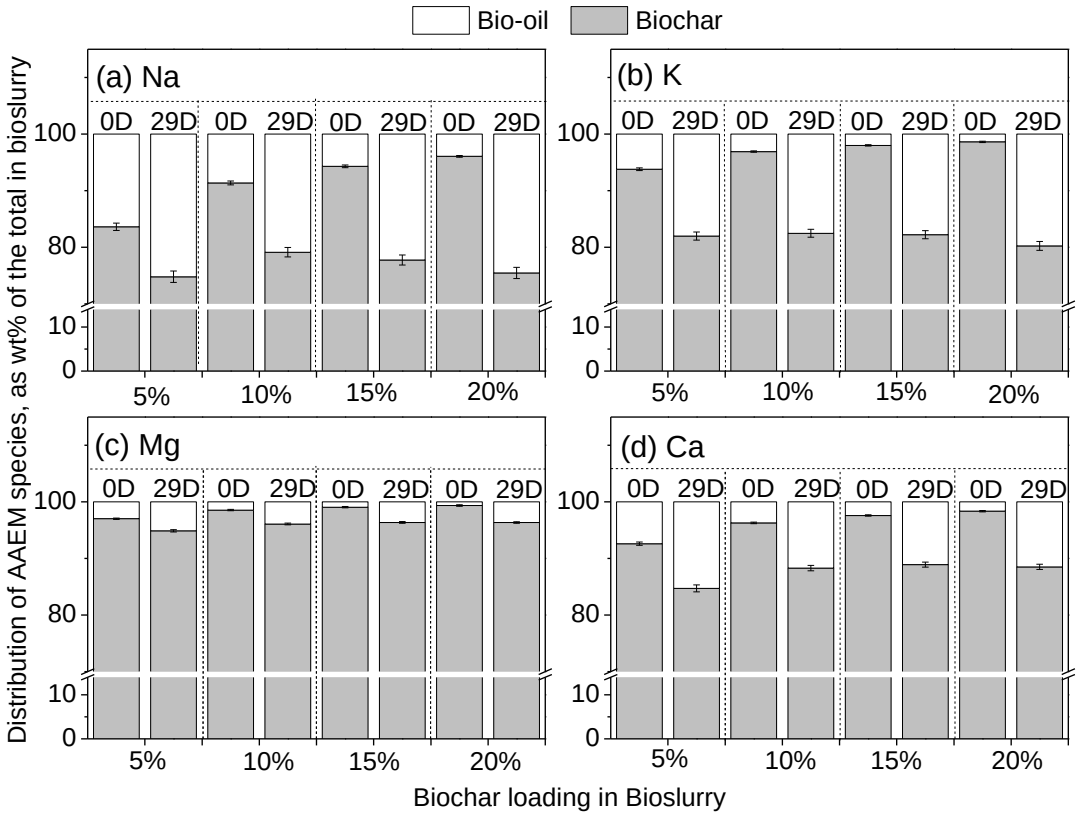

Figure 5-10 Distribution of Na, K, Mg and Ca between biochar and bio-oil phase within bioslurry samples prepared from bio-oil A at various biochar loading levels of 5, 10, 15 and 20% (based on weight). Legend: 0D, after storage for 0 day; 29D, after storage for 29 days

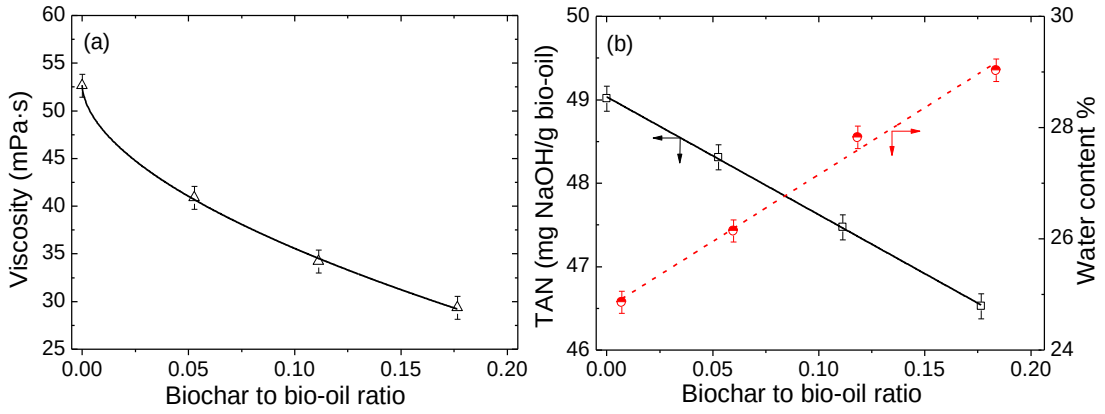

Figure 5-11 Viscosity, water content and TAN of bio-oil phase as a function of the biochar/bio-oil ratio (based on weight) in bioslurry prepared from bio-oil A (after storage for 29 days)

The results reported in this study have some important implications. Even at room temperature, the storage of bioslurry clearly leads to the ageing of the fuel, resulting in reductions in TAN and viscosity of the bio-oil phase, an increase in water content of the bio-oil phase and the leaching of AAEM species from the biochar into the bio-oil phase. The presence of biochar makes the ageing of bioslurry fuels more severe. The reduction in the viscosity of the bio-oil in bioslurry is favourable to the atomisation of bioslurry fuels.[22,29] The reduction in TAN of the bio-oil phase in bioslurry fuels is also favourable.[18] However, even at 15% biochar loading, after storage for 29 days, the bio-oil phase is still acidic. It is well-known that the release of inherent AAEM species is one of the major concerns related to the combustion of biomass-based fuels, because of ash-related issues such as fouling, sintering, deposition and particulate matter (PM) emissions.[37,136,139,208,247] Therefore, the significant leaching of AAEM species from the biochar into the bio-oil phase during bioslurry storage causes at least two undesired consequences during practical applications of bioslurry fuels. One is that the AAEM species in biochar leached into bio-oil phase would be prone to be released as part of volatiles, resulting in an increase in fine PM emission (particularly PM_1 emission[139]) during bioslurry combustion. The other is that the AAEM species are known to be good catalysts for biochar/biomass combustion/gasification,[36,248,249] the leaching of

these inherent species from biochar leads to unwanted loss of catalysts for combustion/gasification reaction, hence adverse effects on biochar reaction kinetics.

5.6 Conclusions

This study reports the experimental data on fuel properties evolution and ageing of bioslurry during storage. Biochar has a significant influence on the changes in fuel properties of the bio-oil phase in bioslurry. While the blank bio-oil samples showed negligible change, the presence of biochar in the bioslurry fuels leads to significant changes in fuel properties during 29 days of storage. The reduction of the TAN and viscosity, and the increase of the water content were observed in the bio-oil, at least partially because of some condensation reactions among bio-oil compounds catalysed by the biochar or reactions between the acidic bio-oil and the basic biochar. An increase in biochar loading level leads to further reduction in the TAN and viscosity, and increase in the water content in the bio-oil phase during bioslurry storage. Bislurry storage also leads to undesired redistribution of AAEM species between the biochar and bio-oil phase. The leaching of these inorganic species into the acidic bio-oil phase follows two-step kinetics.

CHAPTER 6 LEACHING CHARACTERISTICS OF ALKALI AND ALKALINE EARTH METALLIC SPECIES FROM BIOCHAR BY BIO-OIL MODEL COMPOUNDS

6.1 Introduction

In Chapter 5, it was observed that there was undesired migration of inherent inorganic species, particularly alkali and alkaline earth metallic (AAEM) species, from biochar into bio-oil phase during bioslurry storage. This redistribution of AAEM species between biochar and bio-oil phase may result in loss of catalysts for combustion/gasification reactions of biochar.[36,248,249] It may also impact ash-related issues (e.g., fine particulate matter emission[139]) during bioslurry combustion because AAEM species in bio-oil phase are readily released into the gaseous phase. Acid and water are known to be effective in leaching some of the inherent AAEM species in biochar.[36,250,251] It was speculated that the water and organic acids in bio-oil may be responsible for this unwanted redistribution of inorganic species between biochar and bio-oil. However, the fundamental mechanisms are still largely unclear, and further investigation of the leaching behaviour of AAEM species in biochar by bio-oil is warranted. Bio-oil is a complex mixture, which contains hundreds of compounds, including water and acids.[34] It is important to understand the leaching capability of these model compounds and their interactions. Identification of the key components in bio-oil responsible for the leaching of AAEM species from biochar in a bioslurry system will also help develop effective methods to minimize the undesired redistribution of AAEM species during bioslurry storage.

Consequently, this chapter focuses on further investigation into the leaching characteristic of AAEM species from biochar to bio-oil in a bioslurry system. A

systematic set of experiments was carried out via mixing biochar with key bio-oil model compounds, bio-oil and the bio-oil water soluble fraction for leaching study. Table 6-1 shows the properties of bio-oil A, water soluble fraction of bio-oil A and the biochar samples used in this chapter.

Table 6-1 Properties of the biochar, bio-oil and bio-oil water soluble fraction used in Chapter 6

Samples	Bio-oil	Bio-oil water soluble fraction	Biochar
Proximate analysis			
Water content (wt%, ar[a])	22.8	nd[c]	1.7
Ash (wt%, db[b])	nd[c]	nd[c]	5.1
Volatile matter (wt%, db[b])	nd[c]	nd[c]	22.0
Fixed carbon (wt%, db[b])	nd[c]	nd[c]	72.9
Elemental analysis (wt%)			
C [a,d]	44.83	12.85	81.65
H [a,d]	6.15	9.81	2.64
N [a,d]	0.19	0.04	0.08
O[e]	48.83	77.30	15.63
Na[b]	0.0001	<0.0001	0.0097
K[b]	0.0012	0.0007	0.3192
Mg[b]	0.0002	0.0001	0.1181
Ca[b]	0.0014	0.0009	0.3074
TAN[f] (mg NaOH/g)	48.6	25.1	

[a] as received basis for bio-oil. [b] dry basis. [c] not determined. [d] dry and ash free basis for biochar. [e] by difference. [f] total acid number.

6.2 Leaching of AAEM Species from Biochar by Bio-oil Model Compounds

The composition of bio-oil depends on production condition and feedstock.[34,54] However, the chemical compounds present in bio-oil can be generally grouped into several categories such as acids, alcohols, ketones, aldehydes, and phenolic compounds.[34] Apart from water which is the most abundant single components, formic acid, acetic acid, methanol, acetone and guaiacol which are present in bio-oil in appreciable amount, [34] are also selected as bio-oil model compounds in this study. It

should be pointed out that the acids here were prepared in water solution at a concentration of 0.01M, which has similar acidity to bio-oils.[184]

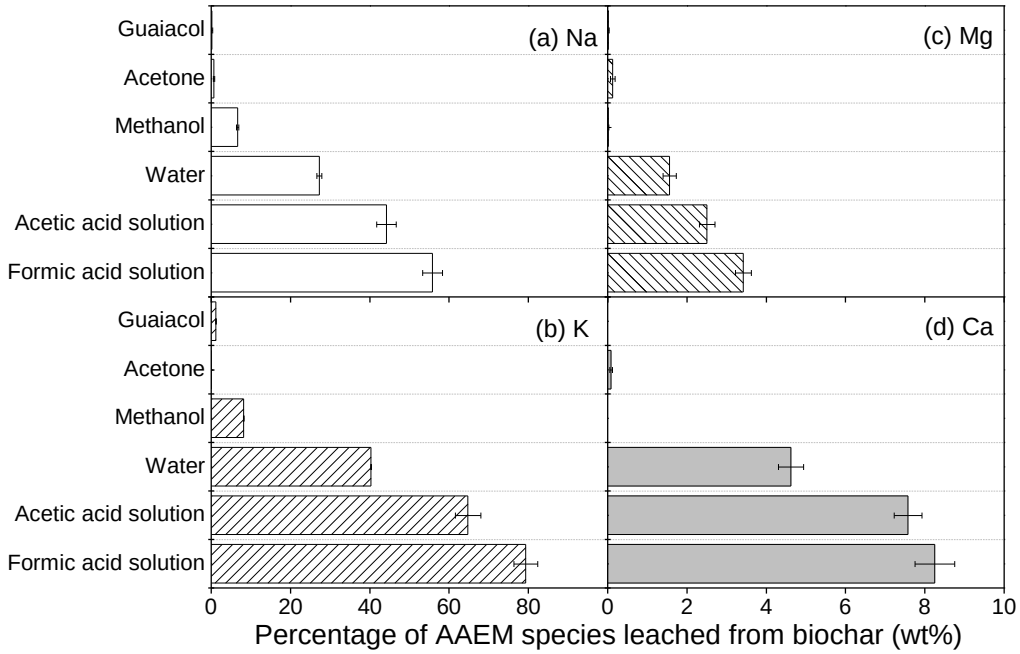

Figure 6-1 Percentage of AAEM species leached from biochar by several bio-oil model compounds. The concentration of acid solutions is 0.01M

Figure 6-1 shows the data on the leaching of AAEM species from biochar by selected bio-oil model compounds. It can be seen that the AAEM species (i.e. Na, K, Mg and Ca) leached by acid solutions and water is significantly higher than that by methanol, acetone or guaiacol. There are more AAEM species leached out by acidic solutions (i.e. ~44 and 56% of Na, ~65 and 80% of K, ~3 and 4% of Mg, ~8 and 9% of Ca for acetic acid and formic acid respectively) than those by water (~28% of Na, ~40% of K, ~2% of Mg and ~5% of Ca). This is due to the leaching of AAEM species in organically bound form via ion exchange, in addition to that in water soluble form.[243,252] The higher percentage of AAEM species leached by formic acid solution than that by acetic acid solution indicates the significance of acid strength on leaching capability. This is consistent with our previous observation on less leaching of AAEM species from biochar by bio-oil with higher TAN than that by bio-oil with lower TAN (see

Chapter 5). However, the reasons are largely unknown on why organic solvent is less effective in the leaching of AAEM species than water and why methanol is relatively more effective than the other organic compounds.

Further efforts were then taken to investigate the occurrence form of Na and K species leached out by methanol. Biochar was first leached by water or acetic acid solution. The water–washed biochar and acetic acid–washed biochar were subsequently leached by methanol. The amount of Na- and K- leached by methanol from the water–washed biochar and the acetic acid–washed biochar was analysed. In addition, the water solubility of the Na and K containing species in methanol leachate from the raw biochar was examined by evaporating the leachate and then dissolving the residue in water for IC analysis. The results were benchmarked against the percentage of Na and K leached directly by methanol from the raw biochar (see Figure 6-2). It can be seen that nearly all the Na and K species leached by methanol from the raw char are in water soluble form. The percentage of Na and K species leached by methanol from the acetic acid–washed biochar is slightly lower than that from the water–washed biochar (~5% Na and ~5% K), which is then lower than that from the raw biochar (~7% Na and ~9% K). This indicates that the Na and K species leached by methanol are in water soluble forms (e.g., salts) and/or organically bound forms. However, the data show that significant proportion of Na and K species that is inaccessible by water or even acetic acid has been leached out by methanol. This is likely due to the effectiveness of methanol in dissolving/releasing/removing at least some of pore-blocking matters such as tars and/or soot deposited on biochar during fast pyrolysis in drop-tube/fixed bed reactor.[250] These Na and K species might be either bound with these soot or tar materials or leached from the internal pore system within the biochar after pore opening. Figure 6-3a compares the UV–fluorescence spectra of the leachates from biochar washing using acetic acid solution, water, methanol and acetone. It can be seen there are two peaks in the UV spectrum for the methanol leachate and one peak in the UV spectrum for the acetone leachate. The first peak at low wavelength of 270–290

nm likely corresponds to a one aromatic ring system, while the other peaks at higher wavelength corresponds to more condensed aromatics.[215] These aromatics may be from dissolution of carbon structure of biochar or soot/tar released from biochar pores. However, there is no peak present in the UV spectrum for the water and acetic acid solution leachates. This is reasonable because water and acetic acid solution are ineffective in dissolving/releasing/removing pore-blocking organic matters; hence some water soluble AAEM species within the closed pore systems may be not accessible. The data show that at least some of the deposited tars and/or soot in the biochar pore systems can be removed by organic solvents such as methanol, and hence, increase the accessibility of AAEM species within biochar.

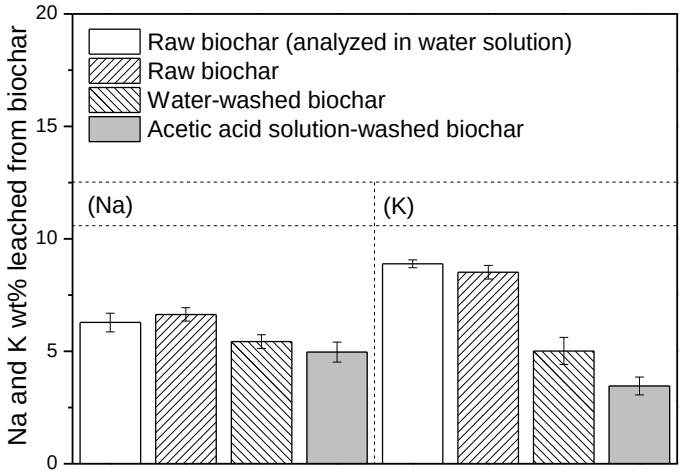

Figure 6-2 Percentage of Na and K species leached by methanol from raw, water–washed and 0.01M acetic acid solution–washed biochars

Therefore, the effectiveness of organic solvents for the leaching of inherent AAEM species in biochar can be due to two factors. One is the occurrence of AAEM species e.g., ionically bound or organically bound, and the solubility of these ionically or organically bound AAEM species in an organic solvent. Low salt solubility is likely to be the main reason for the low leaching capability of organic solvent compared to that of water (see subsequent discussion in Section 6.3). The other is the ability of the

organic solvent to dissolve/release/remove pore-blocking organic matters. This may be related to the solvent properties including polarity and swelling ability to biochar (determined by the molar volume of solvent[253]). Because the molar volume of acetone is higher than that of methanol, the accessibility of acetone towards biochar might be lower. This is supported by the fact that only one peak at higher wavelength region with relatively low intensity was observed for acetone leachate compared to methanol leachate (see Figure 6-3a).

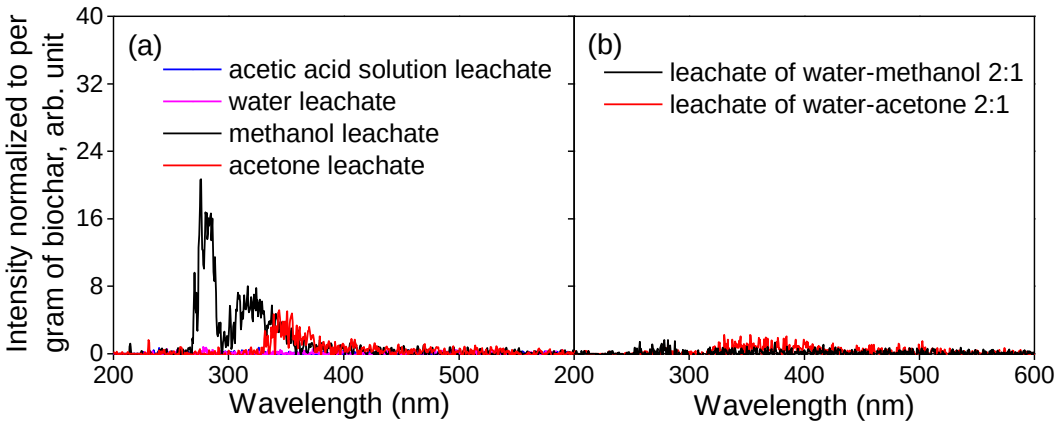

Figure 6-3 UV–fluorescence spectra of leachates of (a) bio-oil model compounds and (b) water–organic mixtures. The ratio 2:1 represents mass ratio of water to organic in the mixture

6.3 Effects of Methanol, Acetone and Phenolic Compounds on the Leaching of AAEM Species by Water

From Section 6.2, we can see that individually, methanol, acetone and guaiacol are not very effective in leaching AAEM species from biochar compared to water. However, how the presence of these organic chemicals will affect the leaching capability of water in a bio-oil system is unknown. Various concentrations of aqueous solutions (as shown in Table 6-2) were prepared to investigate the influence of organics on water leaching. And it should be noted that the liquid to biochar ratios were adjusted to

maintain the water to biochar ratio at 20:1 in all experiments (see Table 6-2). Figure 6-4 shows the data on the leaching of AAEM species from biochar by various water–methanol (and/or) –acetone mixtures, benchmarking against that by water directly. It can be seen from this figure that the percentage of AAEM species leached from biochar decreases with the increase of methanol or acetone addition, especially for Na and K species. After one third of methanol or acetone is added, the percentage of Na species leached from biochar by the water–methanol or water–acetone mixture decreases by ~8 or ~12% respectively while the percentage of K species leached from biochar decreases by ~8 and ~21% respectively. When one third of methanol and acetone is added together into water, the percentage of AAEM species leached from biochar by the mixture decreases by ~15, ~25, ~1 and ~4% for Na, K, Mg and Ca respectively. The presence of methanol or acetone may lead to two possible effects. One is that organic solvent especially methanol might dissolve/release/remove tars and/or soot from pores of biochar, thereby increasing the accessibility of some AAEM species by water (see discussion in Section 6.2). The other is that organic solvent may lower the solubility of ionic salts in water, thus hindering the leaching of AAEM species from biochar by water. As shown in the UV–Fluorescence spectra of leachates of water–methanol and water–acetone mixtures in Figure 6-3(b), these water–organic solutions are ineffective for the removal of aromatics from biochar, suggesting the solvation of methanol or acetone in water solution and poor affinity of these aromatics to water.[254,255] Therefore, the effect of organic solvent on salt solubility in water is most likely to be the dominating factor for the observed decrease in the leaching capability of these mixtures.

Table 6-2 Composition and liquid/biochar ratio of aqueous samples used in Section 6.3

aqueous solution (mass ratio)					aqueous solutions (mol/L)			
sample No.	water	acetone	methanol	liquid/ biochar ratio	sample No.	acetic acid	guaiacol	phenol
1	20	1		21:1	1		0.01	
2	2	1		30:1	2		0.02	
3	20		1	21:1	3			0.01
4	2		1	30:1	4	0.01	0.01	
5	4	1	1	30:1	5	0.01	0.02	
6	2	1	1	40:1	6	0.01		0.01

Dissolution of ionic compounds in a solvent can take place when intermolecular forces between ionic compounds and solvent themselves match or the interaction between ionic compound and solvent is stronger than the interaction between themselves.[256] The intermolecular force of ionic compound is proportional to the amount of charge on each interacting atom (q) and inversely proportional to the distance (d) between them and the dielectric constant (ε) of solvent, as indicated by ($q_1q_2/(d^2\varepsilon)$).[257] Therefore, it is well known that the solubility of ionic compound decreases with decreasing dielectric constant of solvent, as results of increasing intermolecular force of ionic compounds.[256] The dielectric constant ε of methanol (33.3) or acetone (21.3) is much lower than that of water (80.0).[256] The dielectric constant ε of methanol–water and acetone–water mixtures decreases with increasing organic concentration.[258] This leads to decreases in the solubility of salt in methanol- or acetone- containing mixtures hence decreases in the leaching of AAEM species from biochar by these water–solvent mixtures. The dielectric constant ε of methanol is higher than acetone, so that the interactions among methanol and water molecules are more closer compared to those among acetone and water molecules because of hydrogen bonding.[256] Therefore, the

negative effect of methanol seems to be less than that of acetone on water leaching, especially for Na and K species (as results of a reduced effect on salt solubility). Because of the nonlinear influence of ions on the dielectric constant of the mixtures,[259] the adverse effect of methanol or acetone on leaching of AAEM species (especially Na and K) from biochar may not be proportional to the increase in solvent addition.

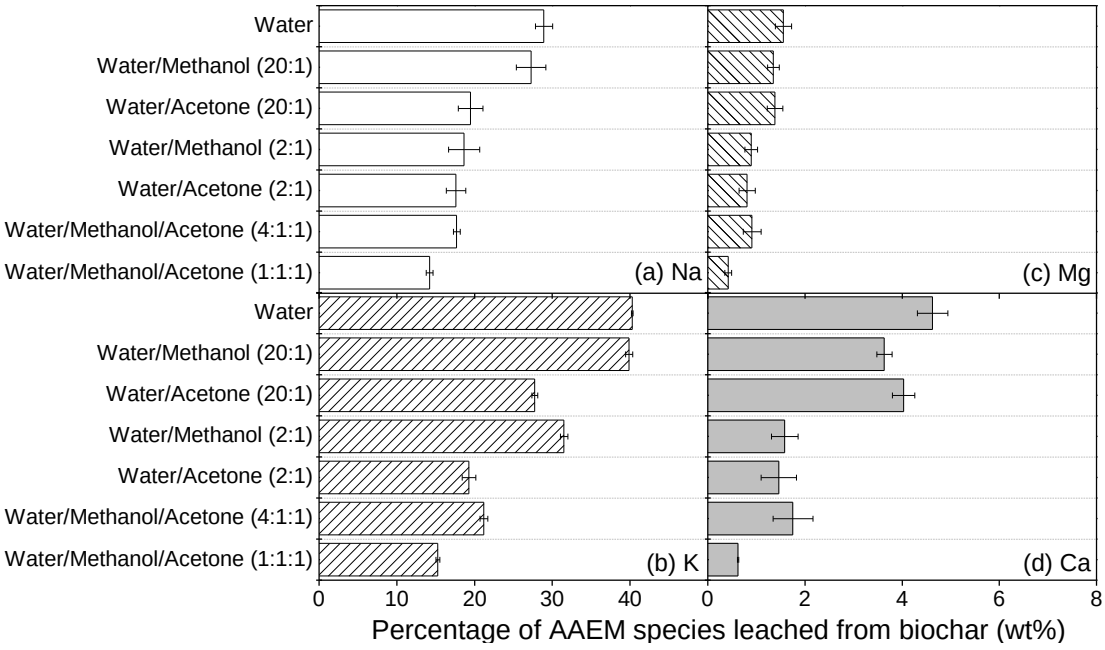

Figure 6-4 Percentage of AAEM species leached from biochar by water and water–methanol (and/or) –acetone mixtures. The ratio in parenthesis represents the mass ratio of water/organic in the mixture outside of the parenthesis

Further efforts were taken to investigate the effect of phenolic compounds on water or acetic acid solution leaching using guaiacol and phenol as model compounds. The composition of phenol and guaiacol solutions can be found in Table 6-2 and the results from leaching experiments are presented in Figure 6-5. The percentage of Na and K species leached from biochar is ~14 and ~8% of Na, ~16 and ~8% of K for 0.01 M phenol in water solution and 0.01 M guaiacol in water solution respectively, which is lower than that leached by water alone. However, the percentage of Mg and Ca leached by phenolic water solutions is nearly the same as that leached by water alone.

Similar phenomena, i.e. reduction in leaching of Na and K species and little change in leaching of Mg and Ca species by addition of phenol or guaiacol, was also observed for acid solutions. The reasons for the different influence on leaching of Ca, Mg species and Na, K species may be attributed to two aspects. On the one hand, the presence of phenolic compounds in aqueous solution can lower the dielectric constant ε of the mixture [260,261] thereby reducing the salt solubility in water (see discussion in last paragraph). However, in comparison to that of monovalent ionic compounds, the solubility of divalent ionic compounds in the solutions is less influenced by the presence of phenolic compounds because of stronger interactions among divalent ions and phenolic compounds.[262,263] On the other hand, phenolic compounds may penetrate into biochar and act as promoter for leaching of AAEM species. It was previously reported that phenolic compounds in bio-oil can act as promoter for the leaching of AAEM species (especially Mg and Ca) from biomass.[264] While the exact mechanisms are largely unknown, such an effect was attributed to the increased permeation of phenolic compounds into the organic matrix of biomass. This leads to an increase in the accessibility of water and acid to biomass matrix hence an increase in the leaching of AAEM species.[264] Similarly, permeation of phenolic compounds into the biochar is supported by the relatively lower intensity of the UV−fluorescence spectra of the leachates of phenolic compounds solutions in comparison to that of the blank solutions (as illustrated in Figure 6-6a). The more prominent permeation of phenol into biochar may contribute to the higher percentage of Na and K species leached by phenol solutions compared to that by guaiacol solutions. Therefore, for Ca and Mg, the negative effect on solubility of Ca and Mg salts appears to be overcome by the promotion effect on the penetration of phenolic compounds into biochar, while for Na and K, the hindering effect on solubility of Na and K salts still dominates. In addition, the difference between the leaching capability of 0.01 M and 0.02 M guaiacol solutions is negligible. This might be due to the fact that the concentration difference is not sufficient to introduce an obvious solubility change of AAEM species or the

promotion effect caused by penetration is already saturated at a concentration of 0.01M for guaiacol solutions.

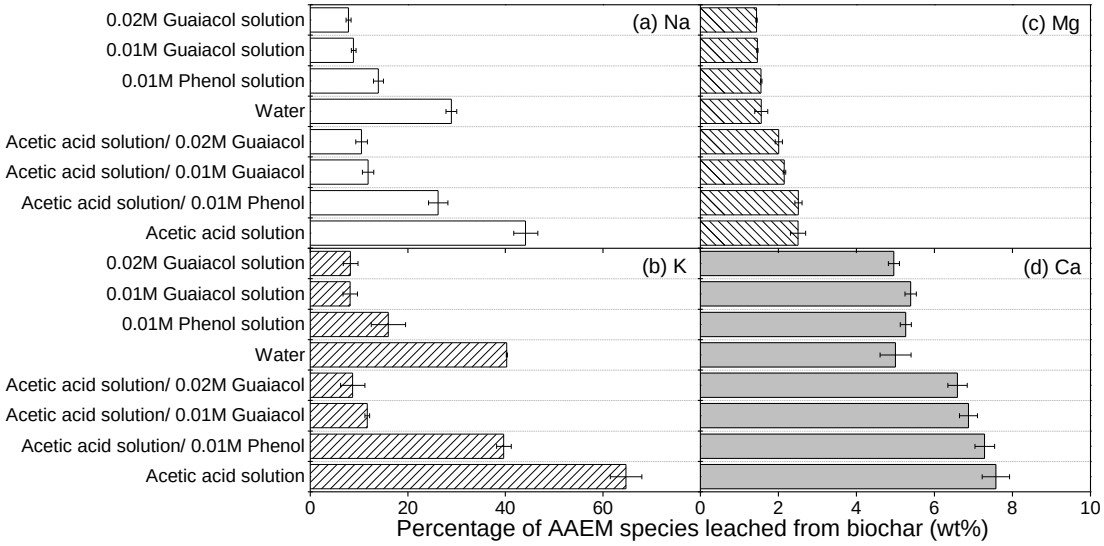

Figure 6-5 Percentage of AAEM species leached from biochar by phenol solutions and guaiacol solutions. The concentration of acid solutions is 0.01M

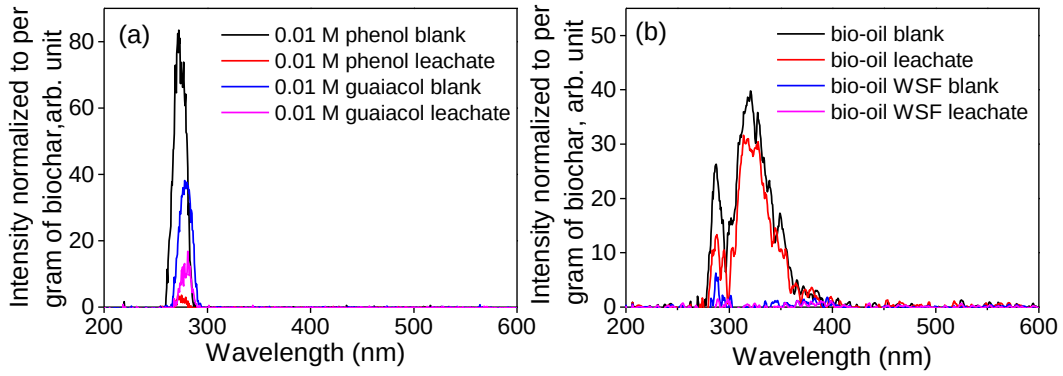

Figure 6-6 UV–fluorescence spectra of blank and leachate of (a) phenol solution and guaiacol solution and (b) bio-oil and bio-oil water soluble fraction (referred to as "bio-oil WSF"). Bio-oil samples were diluted in methanol at 4 ppm to avoid self-absorption; phenol solution and guaiacol solution were diluted in water at concentration of ~0.25 wt% to avoid flat top on the instrument

6.4 Leaching of AAEM Species from Biochar by Bio-oil Water-Soluble Fraction and Further Discussion

Water addition for fractioning bio-oil is widely used for bio-oil characterization and investigations.[20,107,265] Bio-oil can be separated into water soluble fraction and insoluble fraction based on water solubility of different bio-oil components. As the water insoluble fraction of the bio-oil is a sticky viscous layer and difficult to mix with biochar, only the water soluble fraction is investigated, benching against the raw bio-oil and water in this study.

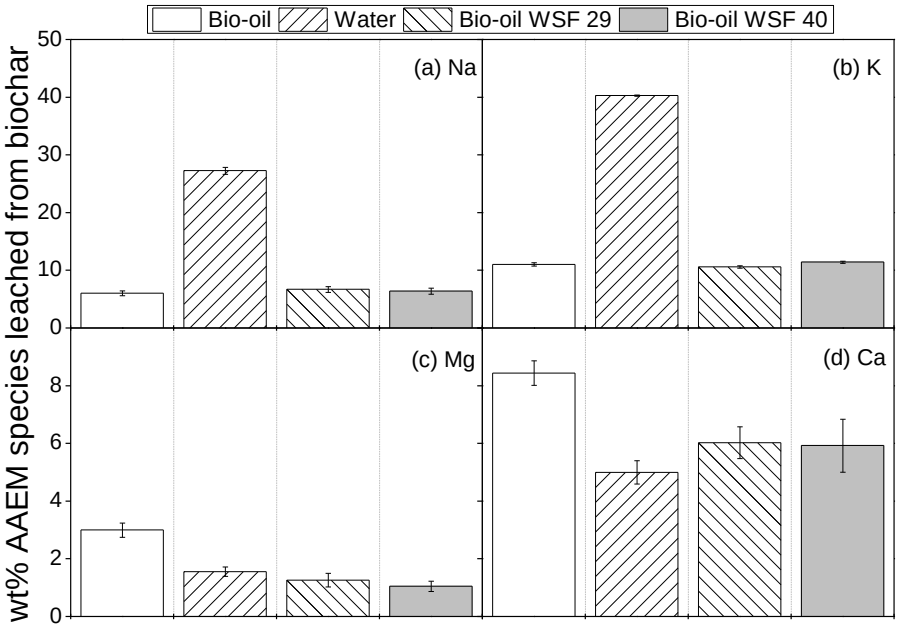

Figure 6-7 Percentage of AAEM species leached from biochar by bio-oil water soluble fractions bench against that by bio-oil and water. Bio-oil WSF 29 and bio-oil WSF 40 represent bio-oil water soluble fraction with liquid to biochar ratio of 29:1 and 40:1 respectively

Another two bio-oil water soluble fraction to biochar ratios (i.e. 29:1 and 40:1) were employed in this study for comparison with the ratio of 20:1. Because the added water in the bio-oil water soluble fraction was not evaporated and the proportion of the actual

water soluble components extracted from the bio-oil accounts for ~46% and ~32% of the bio-oil and the water soluble fraction respectively, a calculation indicates that the bio-oil water soluble fraction to biochar ratio of 29:1 can ensure equal water soluble components to biochar ratio as the bio-oil to biochar ratio of 20:1. Meanwhile, the ratio of 29:1 also enables the bio-oil water soluble fraction to be comparable with water as the ratio of water in the bio-oil water soluble fraction to biochar is 20:1. Besides, as the total acid number (TAN) of the bio-oil water soluble fraction is ~50% of that of the bio-oil (see Table 6-1), the bio-oil water soluble fraction to biochar ratio of 40:1 is selected to obtain an equal TAN to biochar ratio as the bio-oil to biochar ratio of 20:1.

Because bio-oil or bio-oil water soluble fraction is acidic containing both water and acids, both of them are expected to be more effective for leaching of AAEM species than water. However, the data in Figure 6-7 show otherwise. The percentage of Na and K species leached by water (~28 and ~40% respectively) is significantly higher than that leached by the bio-oil water soluble fraction (~6 and ~11% respectively), despite the fact that the water/biochar ratio in the mixtures of the bio-oil water soluble fraction and biochar(29:1 or 40:1, w/w) is equal to or higher than 20:1. This suggests that the leaching capability of the water in the bio-oil water soluble fraction is limited. This is likely due to the negative effect of other organic compounds in bio-oil on the leaching process (see discussed in Section 6.3). Similarly, the leaching capability of the bio-oil for Na and K species is nearly the same as that of the bio-oil water soluble fraction. However, the percentage of Mg and Ca species (~3 and ~8% respectively) leached by the bio-oil is slightly higher than that leached by the bio-oil water soluble fraction (~2 and ~6% for Mg and Ca respectively), even though the bio-oil water soluble fraction with a liquid/biochar ratio of 40:1 has an equal TAN to biochar ratio as the bio-oil. This indicates that acidity is not the limiting factor for the relatively low capability of the bio-oil water soluble fraction for leaching of Mg and Ca species. As discussed in Section 6.3, phenolic compounds penetrating into biochar can promote the leaching of AAEM species especially Ca and Mg species. Likewise, permeation of the bio-oil and

bio-oil water soluble fraction is observed by the relatively lower intensity of the leachates of the bio-oil and bio-oil water fraction compared to the blanks in the UV−fluorescence spectrum (see Figure 6-6b). However, there is only one peak at wavelength of 270–290 nm corresponding to a one aromatic ring system (see Section 6.2) detected for the bio-oil water soluble fraction, while there are two peaks detected for the bio-oil. Additionally, the peak intensity of the bio-oil water soluble fraction is significantly lower than that of the bio-oil. Therefore, the relatively higher percentage of Mg and Ca species leached by the bio-oil compared to that by the bio-oil water soluble fraction is at least partially due to the relatively high content of one aromatic ring compounds or the presence of more condensed aromatics.

On the basis of all of the results obtained in this study, it is fair to conclude that leaching of AAEM species (i.e. Na, K, Mg and Ca) from biochar by bio-oil is mainly attributed to acids and water in water soluble fraction of bio-oil, while the leaching capability of other organics may vary because of their properties such as polarity or dielectric constant. However, the effects of other organics on leaching capability of water or acid are non-negligible. Generally, organic compounds (except acids) with lower polarity or dielectric constant than water can hinder the leaching of Na and K species. However, leaching of Ca and Mg species may be enhanced if promotion effect of phenolic compounds is adequate. Therefore, by adding an appropriate solvent in a bioslurry system, the undesired redistribution of AAEM species may be minimized. For example, acetone and methanol have both been reported to be able to improve the properties of bio-oil.[29,91,197] However, acetone might be a more appropriate choice for bio-oil upgrading in a bioslurry system because the leaching of AAEM species by acetone is significantly less than that by methanol (see discussion in Section 6.2).

6.5 Conclusions

Inherent alkali and alkaline earth metallic (AAEM) species in a bioslurry system can be migrated from biochar into the bio-oil phase via the leaching process. It was found that acids and water in the bio-oil water soluble fraction is responsible for the majority of AAEM species leached from biochar by bio-oil. Other individual organic compounds in bio-oil (e.g., methanol, acetone and guaiacol) have poor polarity or low dielectric constant, so that the capability for leaching of AAEM species seems to be limited. However, the presence of these organic compounds can have significant impact on the leaching capability of water or acids. For example, the presence of organic compounds with low polarity or low dielectric constant can hinder the leaching of AAEM species by water, which can be attributed to the decrease of salt solubility. On the other hand, in the presence of phenolic compounds, the leaching of AAEM species (especially Mg and Ca species) may be enhanced because these phenolic compounds improve the accessibility of AAEM species within the biochar structure by water or acid.

CHAPTER 7 PHASE BEHAVIOUR AND FUEL PROPERTIES OF GLYCEROL/METHANOL/ BIO-OIL BLENDS

7.1 Introduction

As reviewed in Chapter 2, biodiesel is considered to be a renewable liquid transportation fuel and has attracted substantial research and development in recent years.[43,45,144,148,266,267] The rapid growth of biodiesel industry has generated a large surplus of glycerol that is of low market value.[43,45,48-50,144,148,266] In small or medium scale biodiesel plants, the by-product glycerol is usually disposed of as a waste stream due to the high cost for purification.[43,268,269] However, such waste disposal can cause severe environmental concerns and is not economically friendly.[43,46,47,50,270] Therefore, utilization of the huge stockpile glycerol is of great importance to the sustainable development of biodiesel industry. Combustion and gasification are considered as key technologies for glycerol utilisation due to large-scale application, flexibility to directly accommodate the crude glycerol product without refining, and easy integration into biodiesel production process etc.[43,52,53,147,168,169] Unfortunately, direct fuel application of glycerol faces some challenges due to several undesirable fuel properties such as high viscosity and high concentration of certain impurities. One possibility to address the challenges with utilization of glycerol alone as a fuel is to mix glycerol with other fuels to make fuel blends. For example, a previous study[53] blended glycerol with yellow grease for combustion, although the results was not satisfactory mostly due to the difficulties in maintaining a homogenous mixture. Therefore, there is a great need to develop fuel blends with alternative fuels.

A good choice is bio-oil, which is a renewable fuel produced from biomass fast pyrolysis and can find various potential applications.[5,18,24,28,39,193,221,271] Bio-oil contains both polar and nonpolar compounds,[54] so that blending glycerol with bio-oil

may produce feasible fuel blends. Therefore, the motive of this study is to investigate the possibility of blending glycerol with bio-oil for fuel applications. Considering the presence of alcohol (typically methanol) in the crude glycerol from biodiesel production system,[29,34,48,147,272] this chapter focuses on the fundamental research into the phase behaviour, rheological properties, fuel properties and stability of glycerol/methanol/bio-oil blends. The key objective is to work out the feasible range for producing and formulating the glycerol/methanol/bio-oil blends. Table 7-1 presents the properties of bio-oil A, glycerol and methanol used in this chapter.

Table 7-1 Properties of the bio-oil, glycerol and methanol used in Chapter 7

	Bio-oil	Glycerol	Methanol
Ultimate analysis (wt%, daf[a])			
C	42.64	39.13	37.50
H	7.55	8.70	12.5
N	0.22	--	--
O[b]	49.59	52.17	50.00
Water content (wt%, ar[c])	23.5	n.d.[e]	n.d.[e]
Viscosity (25 ℃, cSt)	178.2	694.4[g]	0.8 [g]
Surface tension (25 ℃, mN/m)	35.70	62.87	22.35[h]
Density (25 ℃, g/cm^3)	1.21	1.26[g]	0.78[h]
HHV (MJ/kg)[d]	18.9	18.7	20.8
TAN[f] (mg NaOH/g bio-oil)	49.1	n.d.[e]	n.d.[e]

[a] dry and ash free basis for bio-oil, calculated for glycerol and methanol; [b] by difference; [c] as received basis; [d] calculated high heating; [e] not determined; [f] total acid number; [g] value reported in reference[165] [h] value reported in reference[273]

7.2 Phase Behaviour of Glycerol/Methanol/Bio-oil Ternary System

Solubility of the glycerol/methanol/bio-oil systems is determined via experiments and presented in a ternary phase diagram. As shown in Figure 7-1, the results lead to some important observations. First, either bio-oil or glycerol is miscible with methanol. This observation is consistent with reports in open literatures;[54,95,166] both bio-oil/methanol and glycerol/methanol binary systems are single-phase solutions. Second, for the

binary system of glycerol/bio-oil, no measurable amount of glycerol or bio-oil was found dissolvable in each other. The results are opposite to the initial expectation that some glycerol may be soluble in bio-oil as the water present in bio-oil may be miscible with glycerol.[166] The results in Figure 7-1 show that bio-oil and glycerol blends do not form homogeneous solution. Third, the phase conversion line, which represents the minimum methanol required for making the initial glycerol/bio-oil mixtures in homogenous solutions, clearly divides the ternary diagram into two regions. Blends with compositions below the phase conversion line are not homogenous. Addition of more methanol into the system can greatly improve the solubility of glycerol in bio-oil and vice vasa.

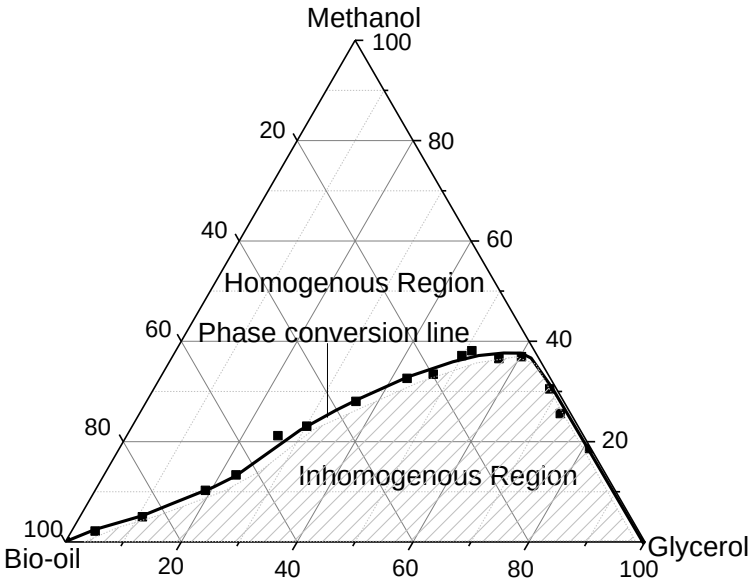

Figure 7-1 Phase diagram of glycerol/methanol/bio-oil ternary system (based on wt %)

The mechanism possibly responsible for the insolubility of glycerol in bio-oil, and the function of methanol addition, is sketched in Figure 7-2, in which the presentation of the bio-oil structure follows the convention used previously (see Garcia-Perez et al[111]). As shown in Figure 7-2a, in the absence of methanol, glycerol molecules tend to attract to each other rather than disperse in bio-oil structure, likely due to the entangled structure of glycerol and the network structure of bio-oil. The strong intermolecular

force (hydrogen bonding) of glycerol and its elongated shape make glycerol become entangled,[51,274] and thereby difficult to disperse unless appropriate amount of compound (s) with comparable intermolecular force could be engaged.[256] Although it is possible for some components of bio-oil (e.g., water) to be individually soluble with glycerol, such accessibility might be low due to a network structure formed by some heavy compounds (e.g., oligomers) in bio-oil.[111,275] On the other hand, methanol as an amphiphilic compound can help the dispersion of glycerol as illustrated in Figure 7-2b. Therefore, with the addition of suitable amounts of methanol, a homogenous mixture can be formulated and prepared. This is also clearly evidenced by the microscopic photographs of glycerol/bio-oil mixtures before and after methanol addition as shown in Figure 7-3.

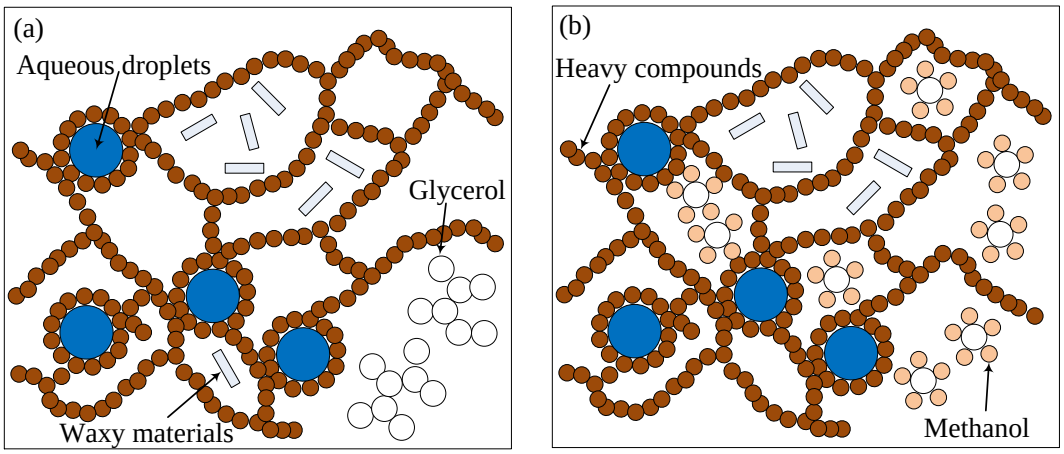

Figure 7-2 Schematic diagrams illustrating the possible solubility mechanism of (a) binary glycerol/bio-oil system without methanol addition and (b) ternary glycerol/methanol/bio-oil system

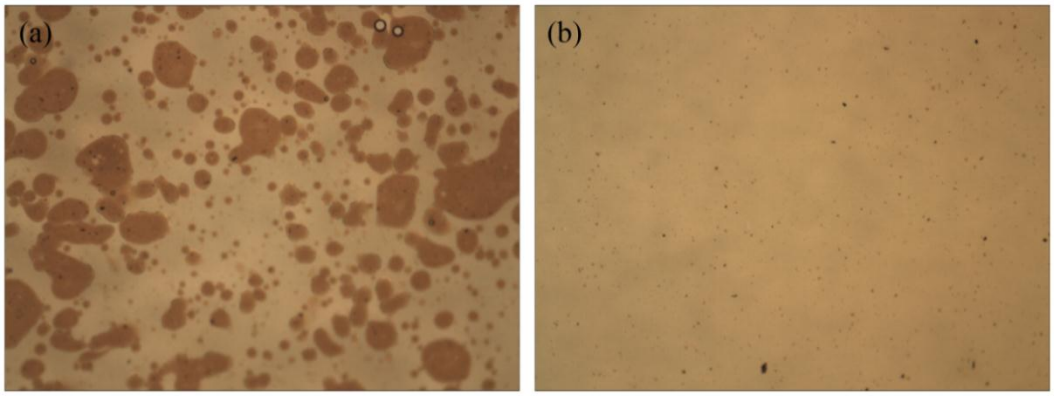

Figure 7-3 Representative microscopic photographs of a glycerol/bio-oil mixture before and after methanol addition. Panel (a) is for a glycerol/bio-oil blend with composition (base on wt %) of 78.8 % bio-oil and 21.2% glycerol. Panel (b) is for a glycerol/methanol/bio-oil blend with composition (base on wt %) of 70.7% of bio-oil, 19.0% of glycerol and 10.3% of methanol

7.3 Fuel Properties and Feasible Range of Glycerol/Methanol/Bio-oil Blends

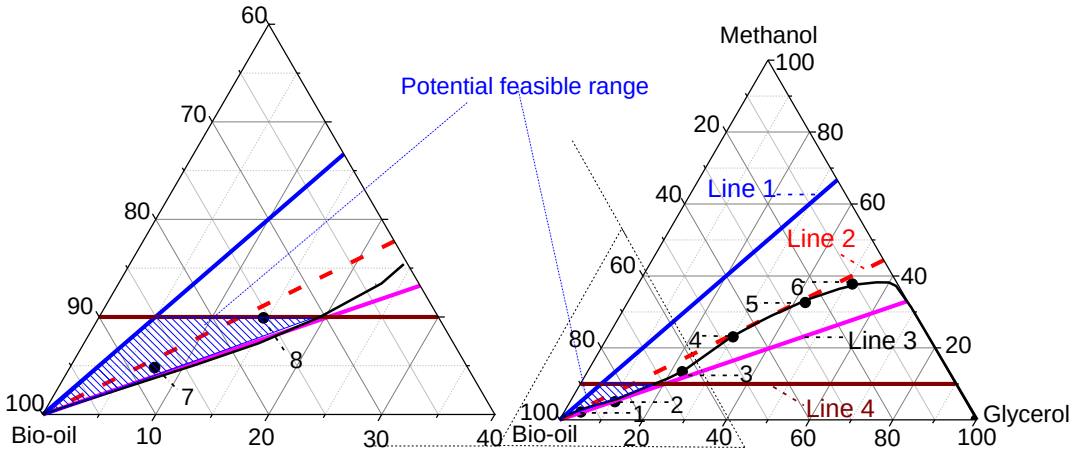

Figure 7-4 Potential feasible range (based on wt %) of glycerol/methanol/bio-oil blend. Lines 1, 2, and 3 represent blends with fixed glycerol-to-methanol ratios of 0.5:1, 1.25:1, and 2:1 respectively. Line 4 represents blends with fixed methanol percentage of 10%. The numbers 1−6 represents the fuel blends (Blend 1−6) on the phase conversion line selected for analysis in section 7.3. The numbers 7and 8 represent Blend 7 and Blend 8 selected from the feasible range for accelerated ageing tests in section 7.4

Table 7-2 Fuel properties of selected fuel blends with compositions located on phase conversion line (wt %, glycerol/methanol/bio-oil)

Fuel blends	Elemental analysis (wt %)[a]				Heating value	Viscosity	Density	Surface tension	Ohnesorge number[a]
	C	H	O[b]	N	HHV (MJ/kg)[a]	(cSt,@25 ℃)	(g/cm^3,@25 ℃)	(mN/m,@25 ℃)	(dimensionless)
Blend 1 (4.3/1.9/93.8)	42.39	7.69	49.72	0.20	18.90	130.1	1.20	35.02	2.9
Blend 2 (10.8/5.0/84.2)	42.00	7.92	49.90	0.18	18.95	90.3	1.19	34.96	2.0
Blend 3 (22.8/13.4/63.8)	41.15	8.47	50.24	0.14	19.08	40.3	1.15	33.33	0.9
Blend 4 (30.1/23.1/46.8)	40.40	9.03	50.47	0.10	19.24	31.0	1.11	33.90	0.7
Blend 5 (42.7/32.6/24.7)	39.47	9.65	50.83	0.05	19.40	36.2	1.05	32.99	0.8
Blend 6 (51.1/38.1/10.8)	38.89	10.02	51.07	0.02	19.48	22.5	1.07	33.21	0.5

[a] calculated value; [b] by difference.

Fuel properties of selected glycerol/methanol/bio-oil blends (blend 1−blend 6) on the phase conversion line in Figure 7-4 are shown in Table 7-2. It can be seen that the HHV of the mixtures slightly increased compared to bio-oil or glycerol alone, which is due to the high HHV of methanol (see Table 7-1) present in the system. The viscosity of the blends ranged from 22.5 to 130.1 cSt (at 25 ℃) which is significantly lower than that of bio-oil (178.2 cSt, 25 ℃) or especially glycerol (694.4 cSt, 25 ℃)[165] alone. This viscosity range is well within the specification of viscosity for No.4 to No.6 fuel oil (26.4–194 cSt, 38 ℃).[276] The density and surface tension of the fuel blend 1−6 ranged from 1.20–1.07 g/cm^3 and 35.02–33.21 mN/m respectively; they are close to or slightly lower than those of bio-oil (1.21 g/cm^3 and 35.70 mN/m respectively) but significantly lower than those of glycerol especially with regard to the surface tension (62.87 mN/m). Viscosity, density and surface tension are three properties most related to the atomization or spray behaviour of fuel. Ohnesorge number calculated from the value of these three properties is an important parameter for predicting the Sauter Mean Diameter (SMD) of a spray droplet, thereby estimating spray or atomization quality.[277] The Ohnesorge numbers of the mixtures, calculated following a method detailed elsewhere,[28] are also listed in Table 7-2. The low Ohnesorge numbers of the blends (0.5–2.9) compared to bio-oil (4.0) and glycerol (11.1) alone implies improved atomization quality of the blend. Overall, the fuel properties of the bio-oil/glycerol/methanol blends even along the phase conversion line are better than bio-oil or glycerol alone, suggesting that these fuel blends are suitable for burner use. The improvement of fuel properties is most likely due to the addition of methanol (with a viscosity of 0.8 cSt and surface tension of 22.35 mN/m at 25 °C[165,273]) Therefore, for the mixtures above the phase conversion line with higher methanol percentage, the fuel properties are expected to be better. However, the high proportion of methanol in the fuel mixture may raise other concerns as discussed below.

First, flash point needs to be considered for safe storage and handling of fuels. Flash point of a mixture system is largely influenced by the component with lowest flash

point.[278] In the case of the glycerol/methanol/bio-oil system, the flash point of methanol (11 ℃) is much lower than that of glycerol (160 ℃) and bio-oil (40–110 ℃);[197] therefore, the flash point of the mixture will be significantly affected by the percentage of methanol. It is well-accepted that addition of up to 10 wt% methanol can improve bio-oil properties without causing significant decline in fuel flash point.[29,197,279] Therefore, likewise, no greater than 10 wt% methanol in the glycerol/methanol/bio-oil system is recommended for safety concerns. Unfortunately, it is known that the available flash point test methods are not suitable for bio-oil samples;[6] flash point tests were not performed in this study.

Second, the ratio of glycerol to methanol can be considered as such binary blend might be obtained from a biodiesel production system, reducing the costs associated with glycerol refining. Figure 7-4 shows that glycerol/methanol blends with a mass ratio between 2:1 and 1.25:1 can be blended with bio-oil in limited proportion (e.g., less than 20 wt% for a ratio of 2:1) to produce homogeneous glycerol/methanol/bio-oil blends. However, glycerol/methanol blends with a mass ratio higher than 2:1 cannot be mixed into bio-oil for producing homogeneous fuel blends and those with a ratio lower than 1.25:1 can be blended with bio-oil in any proportion. In most of commercial biodiesel production systems, molar ratios between 6:1 and 10:1 for methanol to triglycerides (i.e. oil or fat) are commonly used,[61] leading to a theoretical mass ratio of glycerol-to-methanol being 1:1−0.4:1 after transesterification, which means glycerol/methanol blend with such ratios can be mixed with bio-oil in any proportion. However, this ratio may increase in practice due to recovery of methanol and distribution of methanol in biodiesel and glycerol after phase separation. Up to 80% of excess methanol may end up in glycerol phase,[49,280] leading to a theoretically possible glycerol-to-methanol ratio of 1.25:1−0.5:1, and methanol recovery rate can vary. The higher the methanol recovery, the higher the cost put into distillation operation.[281,282] Low recovery of methanol on the other hand can lower the distillation cost and may enhance the purity of the methanol recovered due to low distillation

temperature can be used. Suitable methanol recovery is a trade-off between the economic benefits of producing a glycerol/methanol/bio-oil blend as a burner fuel and the costs associated with methanol recycling and glycerol refining in the biodiesel production system. Nevertheless, based on the assumptions that the low bound of the methanol to triglyceride molar ratio is 6:1, and 80% of excess methanol is left in glycerol layer after separation, it is estimated that a maximum of 37.5% methanol recovery can enable a glycerol/methanol blend with a ratio of 2:1 to be mixed with bio-oil in lower proportion (less than 20%) for producing homogeneous glycerol/methanol/bio-oil blends. Similarly, at the upper bound of methanol-to-triglyceride molar ratio of 10:1, the methanol recovery can be up to 72.8%. Therefore, depending on the process conditions and considering the aforementioned safety reason, a potential feasible blend range (bio-oil $\geq$ 70%; glycerol $\leq$ 20; methanol $\leq$ 10%, on a weight basis) can be obtained (see Figure 7-4) for producing homogeneous glycerol/methanol/bio-oil blends. Such a feasible range has the boundaries of three criteria lines (lines 1, 3 and 4 in Figure 7-4), that is, the lowest theoretically possible glycerol-to-methanol ratio of 0.5:1, the highest glycerol to methanol ratio of 2:1, and the recommended highest 10 wt% methanol in the blends.

7.4 Accelerated Aging of Glycerol/Methanol/Bio-oil Blends

In this section, two fuel blends (blend 7, with composition of 7.5% glycerol, 4.8% methanol and 87.7% bio-oil and blend 8, with composition of 14.6% glycerol, 9.9% methanol and 75.5% bio-oil, on a weight basis) were selected from the blend composition in the potential feasible range in Figure 7-4 for studying the changes in fuel properties of the fuel blends under accelerated aging correlating to one year storage at room temperature. Figure 7-5 presents the flow behaviour of the fuel blends as well as the bio-oil before and after aging. Both of the blends exhibit Newtonian behaviour like the bio-oil does when shear rate is greater than 30 s^{-1}. This observation is consistent with previous studies on flow behaviour of bio-oil;[27] therefore, the

presence of glycerol and methanol in the blend did not change such flow behaviour. The changes in viscosity, water content and TAN of the fuel blends due to ageing are illustrated in Figure 7-6, and the calculated water content and TAN of fuel blend 7 and blend 8 are obtained via direct addition, considering each value of individual fuel compound and the percentage of each individual compound in the fuel blend mixture.

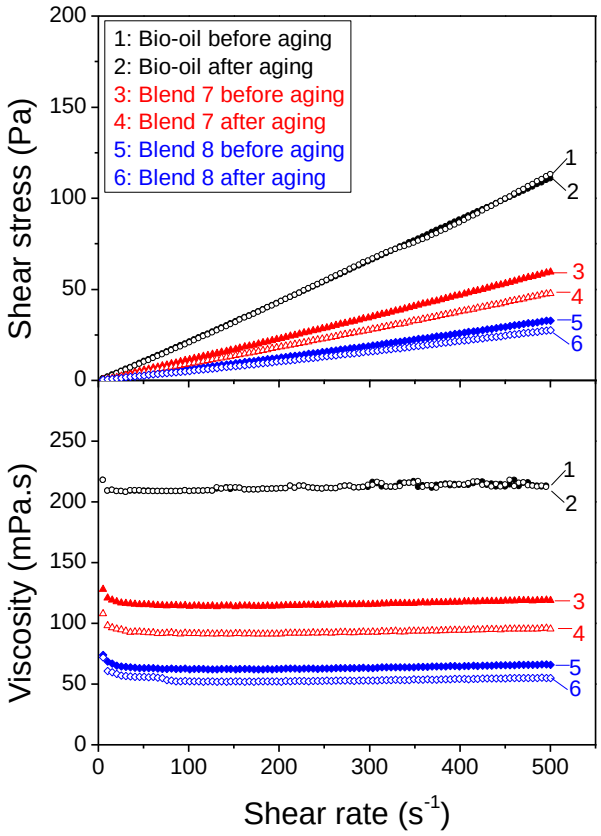

Figure 7-5 Shear stress and viscosity of two glycerol/methanol/bio-oil blends as a function of shear rate (at 25 ℃). Blend 7 is a glycerol/methanol/bio-oil blend with composition (based on weight) of 7.5% glycerol, 4.8% methanol and 87.7% bio-oil. Blend 8 is a glycerol/methanol/bio-oil blend with composition of 14.6% glycerol, 9.9% methanol and 75.5% bio-oil. Aging test was conducted at 80 ℃ for 24 h

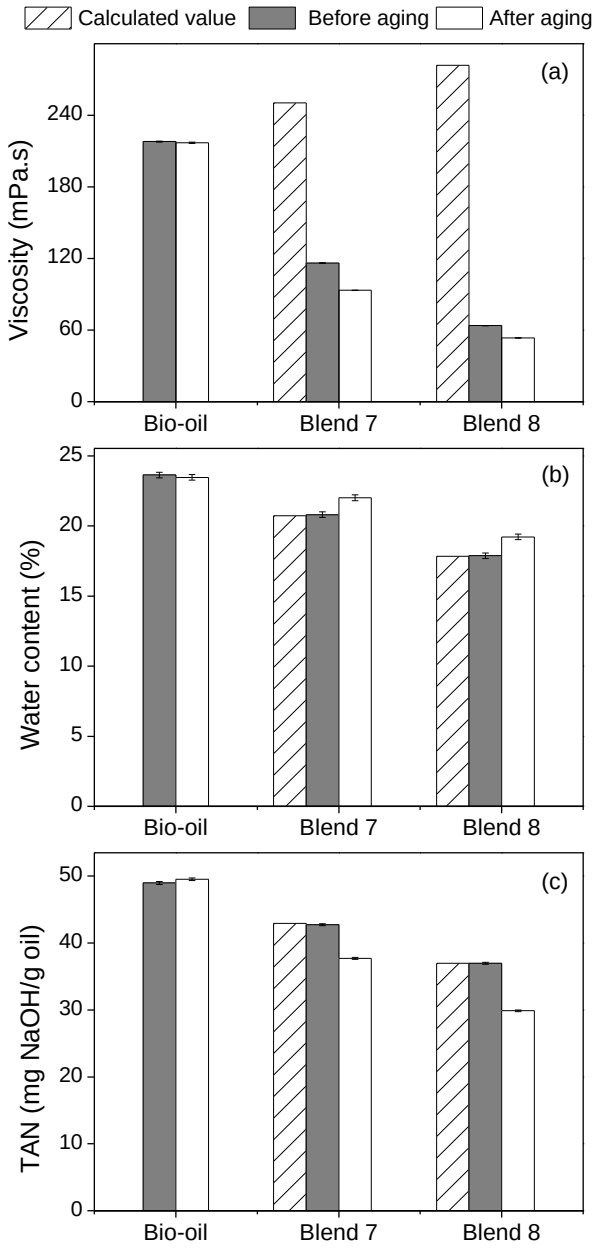

Figure 7-6 Changes in viscosity (a), water content (b) and TAN (c) of two glycerol/methanol/bio-oil blends before and after aging. Blend 7 is a glycerol/methanol/bio-oil blend with composition (based on weight) of 7.5% glycerol, 4.8% methanol and 87.7% bio-oil. Blend 8 is a glycerol/methanol/bio-oil blend with composition of 14.6% glycerol, 9.9% methanol and 75.5% bio-oil. Aging test was conducted at 80 ℃ for 24 h

The data in Figure 7-6 show that before ageing, the viscosity, water content and TAN of the glycerol/methanol/bio-oil blends are all lower than those of the bio-oil blank. When comparing the calculated value with the measured value, it can be seen that the decreases of water content and TAN in the mixtures are due to the dilution of bio-oil by glycerol and methanol. The decrease in the viscosity of the glycerol/methanol/bio-oil blends compared to that of the bio-oil before aging is due to the influence of methanol. It is well-known that methanol addition can significantly decrease the viscosity of bio-oil.[29,35,39,197] Substantial viscosity reduction of glycerol upon methanol addition was also reported.[165]

Additionally, Figure 7-6 shows that after ageing, the viscosity, water content and TAN of the bio-oil blank do not experience significant change after accelerated aging due to the long term storage (over 12 months) prior to experiment, which is consistent with previous findings in Chapter 5. However, noticeable changes were found for the glycerol/methanol/bio-oil blends (blend 7 and blend 8). The decrease of viscosity after accelerated aging (see Figure 7-6a) is likely due to the increase of water content (see Figure 7-6b). Both the increase in water content and the decrease in TAN (see Figure 7-6c) imply that there were chemical reactions taking place during accelerated aging. Esterification between acidic compounds in bio-oil and glycerol or methanol is most likely responsible for the decrease of TAN and the increase of water content. However, on the basis of the data in Figure 7-6, a simple calculation as reported in Chapter 5 shows that the water formed by esterification might only account for part of water increase of the mixtures (~25%). To further investigate the possible reactions occurred during aging, the changes in functional groups of the fuel blends before and after ageing were studied via the comparison of FTIR peak height ratios (according to a previous study[33]). Figure 7-7 presents the FTIR spectra and peak height ratios for the fuel blends before and after aging benchmarking against the blank bio-oil. Figure 7-7a shows that the locations of peaks in the FTIR spectra of all fuel samples are similar to those of bio-oil reported previously.[33] Additionally, Figure 7-7b shows that after

ageing, there is a decrease of peak at 1034 cm^{-1} (representing primary alcohol CH_2–OH) and also an increase at 3382 cm^{-1} (representing O–H stretch) of blend 7 and blend 8, as results of reactions consuming methanol and glycerol together with water formation. Another noticeable change is in the C=C stretch represented by peak at 1646 cm^{-1}, suggesting the formation of alkene or conjugate ketone.[33] This is likely due to glycerol dehydration (known to occur under acidic conditions and high temperature[42,283]) that may also contribute to the increase in water content of the fuel blends after ageing.

On the basis of the experiments carried out in this study, the results suggest that it is possible to prepare homogeneous glycerol/methanol/bio-oil fuel blends. Compared with bio-oil or glycerol alone as a fuel, the blend has improved fuel properties in terms of heating value, viscosity, surface tension and density (see section 7.3). The water content and acidity (i.e. TAN) of the fuel blend can be improved compared to that of the bio-oil due to dilution effect. Although fuel properties of the blends may change during ageing, the overall changes are positive (e.g., reduced viscosity and TAN). While the increase in water content may result in reduction in heating value,[39] the increased water content of fuel blend is still lower than that of the bio-oil after accelerated aging (see section 7.4). Therefore, formulation and preparation of glycerol/methanol/bio-oil blends may provide a potential strategy for utilising the surplus glycerol from biodiesel production process.

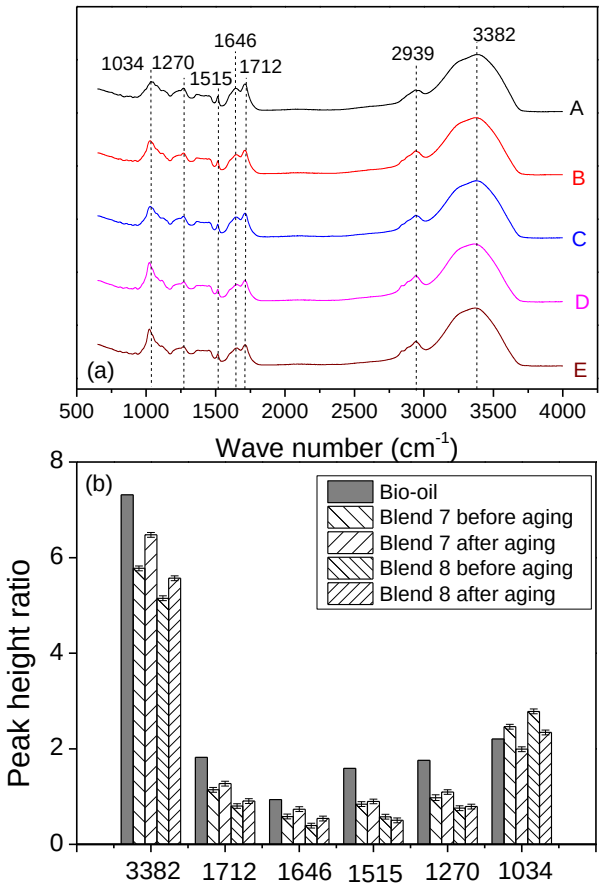

Figure 7-7 FTIR spectra (a) and peak height ratio (b) of two glycerol/methanol/bio-oil blends before and after aging, benchmarking against those of the blank bio-oil. In Panel (a), the FTIR spectra are for (A) blank bio-oil, (B) blend 7 before aging, (C) blend 7 after aging, (D) blend 8 before aging and (E) blend 8 after aging, respectively. Blend 7 is a glycerol/methanol/bio-oil blend with composition (based on weight) of 7.5% glycerol, 4.8% methanol and 87.7% bio-oil. Blend 8 is a glycerol/methanol/bio-oil blend with composition (based on weight) of 14.6% glycerol, 9.9% methanol and 75.5% bio-oil. Aging test was conducted at 80 ℃ for 24 h

7.5 Conclusions

Although the solubility of glycerol in the bio-oil is poor, homogenous ternary glycerol/methanol/bio-oil blends can be prepared with the aid of methanol addition. The fuel properties of such blends including heating value, viscosity, surface tension etc. are improved compared to the bio-oil or glycerol as an individual fuel. Considering safe storage and handling of a fuel and the possible glycerol-to-methanol ratio that might be obtained from biodiesel production system, blends with a composition range (bio-oil ≥ 70 wt %; glycerol ≤ 20 wt %; methanol ≤ 10 wt %) are recommended as potential burner fuels. The accelerated aging tests of the fuel blends show that the properties of the fuel blends can change upon long term storage, that is, noticeable decreases in viscosity and TAN accompanied by an increase in the water content.

CHAPTER 8 EFFECT OF MAJOR IMPURITIES IN CRUDE GLYCEROL ON SOLUBILITY AND PROPERTIES OF GLYCEROL/METHANOL/BIO-OIL BLENDS

8.1 Introduction

Chapter 7 showed that blending glycerol with bio-oil (with the aid of methanol) appeared to be a possible approach for producing a liquid fuel mixture with rheological and other fuel properties suitable for stationary combustion application. In the industrial process for biodiesel production, it is known that methanol is present in crude glycerol[150,284] so that crude glycerol from biodiesel production process may be potentially mixed into bio-oil for manufacturing the fuel blends directly. However, in addition to methanol, crude glycerol also contains various other impurities including water, soap, alkaline catalyst etc.[147,150,151,153,159,284,285] How these impurities affect the solubility of glycerol/methanol/bio-oil system is largely unknown.

It is important to understand the influence of impurities on the blending of glycerol and bio-oil, for at least three reasons. Firstly, it provides the fundamental knowledge for potentially blending crude glycerol with bio-oil to produce a liquid fuel blend for stationary applications. If the impurities can be tolerated in production of fuel blends, crude glycerol can be directly used for fuel blending so that the expensive purification process for crude glycerol in the conventional biodiesel production process may be simplified or even eliminated. This may lead to better economic performance of biodiesel production value chain. Understanding the effect of impurities can further help identify the preferable crude glycerol composition for blending with bio-oil, thereby providing guidance on optimising the integration between the biodiesel production process and the fuel blending process. Secondly, if crude glycerol can be

directly mixed with bio-oil to produce fuel blends, it provides an attractive strategy for utilising crude glycerol, addressing the key issues (e.g., high viscosity and low pumpability, high alcohol content, and high content of inorganic species etc.[51-53,168]) associated with using crude glycerol alone as an energy source. Last but not least, it is possible that the fuel blends of crude glycerol and bio-oil may have improved acidity and stability compared to bio-oil, because not only methanol in crude glycerol can improve bio-oil properties[29,91] but also the alkaline catalysts presented in crude glycerol may neutralize the acidic compounds in bio-oil.

Therefore, this chapter aims to investigate the effect of several key impurities in crude glycerol on the solubility and properties of glycerol/methanol/bio-oil blends and further evaluate the possibility of mixing crude glycerol with bio-oil for producing fuel blends. Properties of bio-oil A used in this chapter are listed in Table 8-1. A series of glycerol-impurity mixtures and formulated crude glycerol were prepared for blending with bio-oil for studying mixture solubility, fuel properties, rheological properties and ageing.

Table 8-1 Properties of the bio-oil used in Chapter 8

Elemental analysis, wt%					Viscosity (mPa.s @25 ˚C)	Water content (wt%)	TAN[c] (mg NaOH/g)
C[a]	H[a]	N[a]	O[b]	Na[a]			
42.64	7.54	0.21	49.61	0.0001	130.3	23.7	48.6

[a] as received. [b] by difference. [c] total acid number.

8.2 Compositions of Crude Glycerol

The compositions of crude glycerol are mainly dependent on three key factors.[48,49] The first factor is biodiesel production process. As shown in Figure 8-1, the biodiesel industry deploys two typical processes, i.e. the PSMR (phase separation before methanol recovery) and MRPS (methanol recovery before phase separation)

processes for biodiesel production,[42,62,281,286,287] with the major differences being in the sequence of methanol recovery and separation of biodiesel and glycerol phase. The PSMR process carries out phase separation before methanol recovery while the MRPS process recovers methanol before phase separation. The second factor is the refining process of crude glycerol. If an acidification refining process of glycerol phase is included in process PSMR as demonstrated in Figure 8-1a, the process is referred as PSMR-N with N standing for neutralisation. The composition of the crude glycerol (hereafter referred to as CG2) obtained from a PSMR-N process is relatively consistent in open literature, i.e. 80–85% of glycerol, 6–14% of water and 2–6% of salt.[160-162] In this study, NaCl is used as model compound of salt as NaOH and HCl are commonly used catalyst and acid for acidification refining in biodiesel production process.[42,61] However, in a PSMR or MPRS without a glycerol refining process, the dominant impurities in the produced crude glycerol from the PSMR and MRPS processes (hereafter referred to as CG1 and CG3, respectively) can be different. For example, water content in CG3 is typically considerably higher than that in CG1 due to addition of water to aid phase separation after methanol was evaporated.[281] The third and last factor is feedstock. Free fatty acid (FFA) and water in feedstock oil or fat can result in soap formation under alkaline condition due to saponification reaction, thereby impacting biodiesel quality and crude glycerol composition.[61] Usually, FFA and water contents in feedstock for biodiesel production are restricted to ≤0.5–3% and ≤0.06% respectively.[42,288]

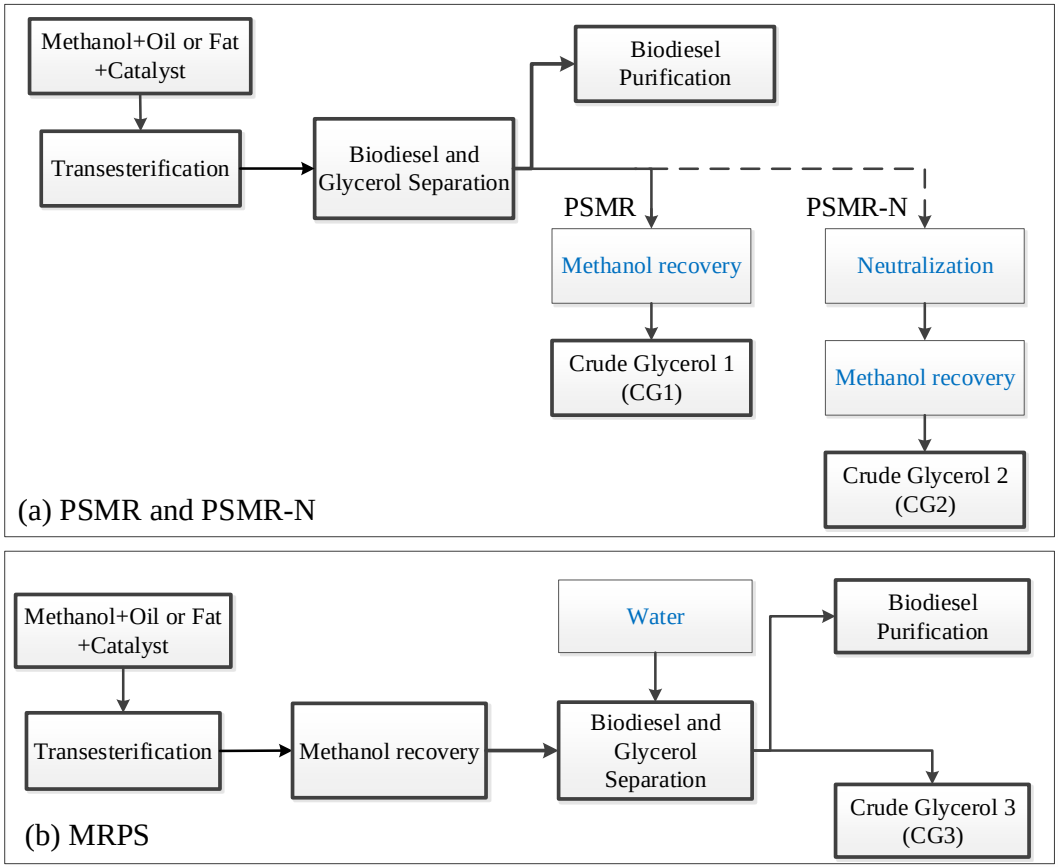

Figure 8-1 Typical biodiesel production processes: (a) the PSMR and PSMR-N processes; (b) the MRPS process. PSMR: (biodiesel/glycerol) phase separation before methanol recovery; PSMR-N: phase separation (biodiesel/glycerol) before methanol recovery with neutralization; MPRS: methanol recovery before (biodiesel/glycerol) phase separation

Based on literature data, the key considerations for formulating the compositions of CG1 and CG3 were then listed in Table 8-2. The first consideration is reactions. Transesterification of vegetable oil (triglycerides) with methanol is the main reaction that can produce biodiesel and glycerol.[63] As excess methanol can drive the reaction to the product side, methanol to oil molar ratio in alkaline catalysed biodiesel production is generally 6:1–10:1 and the conversion rate of oil and yield of biodiesel can be over 98% if optimised conditions (e.g., reaction time, temperature, and mixing rate etc.) are applied.[61,289,290] Therefore, in this study, triolein is used as a model

compound for vegetable oil (triglycerides)[61] and a conversion rate of 98–100% for triolein is considered. Additionally, as unreacted triglycerides prefer to retain in biodiesel phase,[291] triglycerides concentration in crude glycerol is ignored in this study. Also, if FFA and water are present in feedstock oil, hydrolysis of triglyceride to FFA and saponification of FFA can occur under alkaline condition.[61] These reactions are undesirable as it consumes the alkaline catalyst and worsens the product quality.[61] Therefore, water content and FFA content in feedstock are required to be less than 0.06% and 0.5–3% respectively for alkaline catalysed biodiesel production.[42,288] As water content is restricted and the reaction rate of transesterification is higher than hydrolysis,[42] hydrolysis reaction is neglected under the condition studied. However, as alkaline catalyst is usually excessive to convert FFA to soap,[42] a conversion rate of 98–100% same as that of the above transesterification reaction is considered in this study. Furthermore, FFA content in crude glycerol can be lower than 1–1.5%,[48,154] therefore, FFA is regarded as minor impurity in crude glycerol and is not considered in this study. The second consideration is component distribution in crude glycerol during phase separation. Because of polarity similarity, up to 97–99% of soap, 94–97% of catalyst, 99% of water, and 80% of methanol may retain in glycerol phase during phase separation.[49,280,291] The distribution of biodiesel in glycerol phase, on the other hand, may be as low as 0.5% [48] due to the sparing solubility of biodiesel in glycerol. [292] Although phase separation of biodiesel and glycerol may be affected by their mutual solubility and methanol content in the mixture,[292] a simple calculation considering transesterification reaction and methanol to oil molar ratio of 10:1 can indicate that methanol concentration is less than 20% in the final mixture and biodiesel distribution in glycerol phase with such proportion of methanol is negligible according to phase diagram of several glycerol–biodiesel–methanol ternary systems.[293,294] While high soap content may cause difficulty in phase separation of glycerol and biodiesel due to formation of gel,[163] such a difficulty may be addressed

by employing proper separation technique (e.g., centrifuge or long time settling etc.).[290,295] Overall, biodiesel content in crude glycerol is negligible and therefore, not considered in this study. The third consideration is methanol recovery and possible water addition. Methanol recovery in biodiesel production process may be up to 90–94%,[296,297] and if this occurs before phase separation of biodiesel and glycerol, then water is usually added to aid phase separation.[281] Generally, 25–54 mg water addition for 1 g mixture of glycerol and biodiesel was found to be satisfactory,[202] and thereby is used for formulation of CG3 in this study. Therefore, based on the consideration of the feedstock, reaction, product distribution, methanol recovery and water addition in this study, the contents of the unreacted feed oil, FFA and dissolved biodiesel in crude glycerol are minor impurities. The major impurities in crude glycerol are soap, water and NaOH which can account for up to 20, 35 and 10 wt% of the crude glycerol, respectively.

Table 8-2 Key considerations for formulating the compositions of crude glycerol

Parameters	Conditions and considerations
feedstock[42,288]	Vegetable oil is represented by triolein; Free fatty acid (FFA) is represented by oleic acid; 1%≤FFA content ≤3% and water content in feedstock ≤0.06%
methanol to oil molar ratio [61]	6:1–10:1
catalyst [42]	NaOH, 0.3–1.5 wt%
reactions [61,63]	triolein (oil) +3 methanol→3 methyl oleate (biodiesel)+glycerol (98– 100% conversion of oil)
	oleic acid (FFA) +NaOH→ sodium oleate (Soap)+H_2O (98 – 100% conversion of FFA)
methanol recovery [296,297]	94 – 100%
components distribution [48,49,154,280,291,293,294]	catalyst, water and soap in glycerol phase: 97 – 100% methanol in glycerol phase: 80% unreacted oil, FFA and biodiesel in glycerol phase: negligible–1.5%
water addition [202]	25–54 mg/g (biodiesel+glycerol)

Table 8-3 Compositions (wt%) of series of impurity-containing glycerol used in this study

Mixtures	Glycerol	Soap	Water	NaOH	NaCl
GW5	95.0		5.0		
GW15	85.0		15.0		
GW35	65.0		35.0		
GS5	95.0	5.0			
GS20	80.0	20.0			
GW35NaOH2	63.7		34.3	2.0	
GW35NaOH10	58.5		31.5	10.0	
GW15NaCl2	83.3		14.7		2.0
GW15NaCl6 (FCG2)	80.0		14.0		6.0
FCG1-1	80.0	15.0	3.0	2.0	
FCG1-2	87.0	8.0	3.0	2.0	
FCG3-1	60.0	15.0	20.0	5.0	
FCG3-2	67.0	8.0	20.0	5.0	

GW5, GW15 and GW35: glycerol–water mixtures with water contents of 5, 15 and 35% respectively; GS5 and GS20: glycerol–soap mixtures with soap contents of 5 and 20% respectively; GW35NaOH2 and GW35NaOH10: aqueous glycerol solution GW35 with NaOH contents of 2 and 10% respectively; GW15NaCl2 and GW15NaCl6: aqueous glycerol solution GW15 with NaCl contents of 2 and 6% respectively; FCG: formulated crude glycerol.

Based on the above discussion, the experimental program in this paper focuses on the major impurities including soap (represented by sodium oleate[280]), water and alkaline catalyst for the formulation of CG1 and CG3. The formulation considers both a high and a low content (5.0 and 20.0 wt%, 5.0 and 35.0 wt%, and 2.0 and 10.0 wt% for soap, water and NaOH respectively) as seen in Table 8-3 for studying on the effect of individual impurities. Two representative compositions for each of CG1 and CG3, together with one representative composition for CG2, are considered based on the literature data and comparability in this study. The respective impurity-containing crude glycerol samples are also listed in Table 8-3 as FCG1-1, FCG1-2, FCG3-1, FCG3-2 and FCG2, respectively. The major differences between FCG1 and FCG3 are in the contents of water and NaOH (3.0 and 2.0 wt% vs. 20.0 and 5.0 wt%), and

those between FCG1-1 and FCG1-2 or between FCG3-1 and FCG3-2 are in the contents of soap (15.0 wt% vs. 8.0 wt%). Glycerol–water and glycerol–soap mixtures are referred to as "GWxx" and "GSxx" ("xx" represents water or soap percentage in the mixture), respectively. Certain amounts of NaOH or NaCl were added to GW35 and GW15 mixtures respectively to prepare a series of mixtures that are referred to as "GW35NaOHxx" and "GW15NaClxx" ("xx" represents the percentage of NaOH or NaCl in the mixture).

8.3 Effect of Major Impurities in Crude Glycerol on the Solubility of Glycerol/Methanol/Bio-oil System

Solubility of impurity-containing glycerol in the bio-oil is determined by minimum methanol percentage required to obtain a homogenous blend. For the effect of soap and water, the results are benchmarked against the solubility of pure glycerol in the bio-oil, while for the effect of NaCl and NaOH, the results are compared with the solubility of the respective glycerol aqueous solutions. Figure 8-2 shows the minimum methanol required for all the mixtures, as a function of impurity-containing glycerol to bio-oil ratio. Three important findings can be observed from Figure 8-2.

First, Figure 8-2a indicates that when water content of glycerol–water mixture is below 5%, the effect of water on solubility of glycerol in the bio-oil is not obvious. However, the minimum methanol percentage required for dissolving GW35 in the bio-oil is significantly higher than that required for dissolving pure glycerol, especially when the GW35/bio-oil ratio is higher than 1/4. The higher amount of methanol required for obtaining homogenous blend is likely related to phase separation of the bio-oil upon increasing water content in the mixture. It is known that a high water content (e.g., over 30 wt%) can result in phase separation of bio-oil.[39,109] Therefore, the water to bio-oil ratio in the GW/bio-oil mixture was

calculated based on the total water in the mixture including water in bio-oil and water in GW mixture. The results are shown in Figure 8-3a as a function of the GW/bio-oil ratio. It can be seen that the water to bio-oil ratios in the GW5/bio-oil mixtures (GW5/bio-oil ≤1, w/w) are all below 0.3, while those in the GW35/bio-oil mixtures are above 0.3 when GW35 to bio-oil ratio is over 1/4. This suggests that at a water/bio-oil ratio above 0.3 the fuel mixture may result in phase separation of the bio-oil, demanding more methanol for blending. Based on the water content of the bio-oil (~23.7 wt%) and the upper limit water/bio-oil ratio in GW/bio-oil mixture (~0.3), the threshold value of 0.063 can be calculated as a product of GW/bio-oil ratio and the water content of the GW mixture. Such a threshold can be used to predict the maximum water percentage that can be tolerated in crude glycerol without severely worsen the solubility of glycerol in the bio-oil at a fixed GW/bio-oil ratio, or vice versa. For instance, if a GW mixture is required to be blended with the bio-oil in a mass ratio of 1:1, then the water content in the GW solution should not be over 6.3 wt%. Otherwise, more methanol is required to be used as solvent in comparison to the case of blending of pure glycerol and bio-oil.

Second, from Figure 8-2b, it can be seen that the effect of soap on glycerol solubility in the bio-oil is less obvious in the range studied, in comparison to the effect of water. This is expected in consideration of the amphiphilic characteristic of soap. However, it was unsuccessful to blend the GS mixtures into the bio-oil at certain GS to bio-oil ratios (~0.2 and ~0.05 for GS5 and GS20, respectively), even with the aid of methanol. This phenomenon is found to be associated with the presence of excessive soap in the prepared impurity-containing-glycerol/methanol/bio-oil fuel mixture. Based on the data in Figure 8-2b, the soap to bio-oil ratios of the fuel mixtures for which homogenous blends can be achieved were calculated and plotted in Figure 8-3b, as a function of the impurity-containing-glycerol/bio-oil ratio used for preparing the fuel blends. It can be seen in Figure 8-3b that for achieving homogenous fuel blends, the soap to bio-oil ratio is below a threshold value of 0.01.

At soap to bio-oil ratios > 0.01, homogenous fuel blends cannot be achieved. This is most likely due to the formation of micelles in the mixtures, as evidenced in the optical microscope image (see Figure 8-4). Consequently, considering the threshold value of 0.01 for the soap/bio-oil ratio that can be calculated as the product of the GS/bio-oil ratio and the soap content of the GS mixture, it is possible to find the maximum GS/bio-oil ratio at a given soap content of the GS mixture, or vice versa.

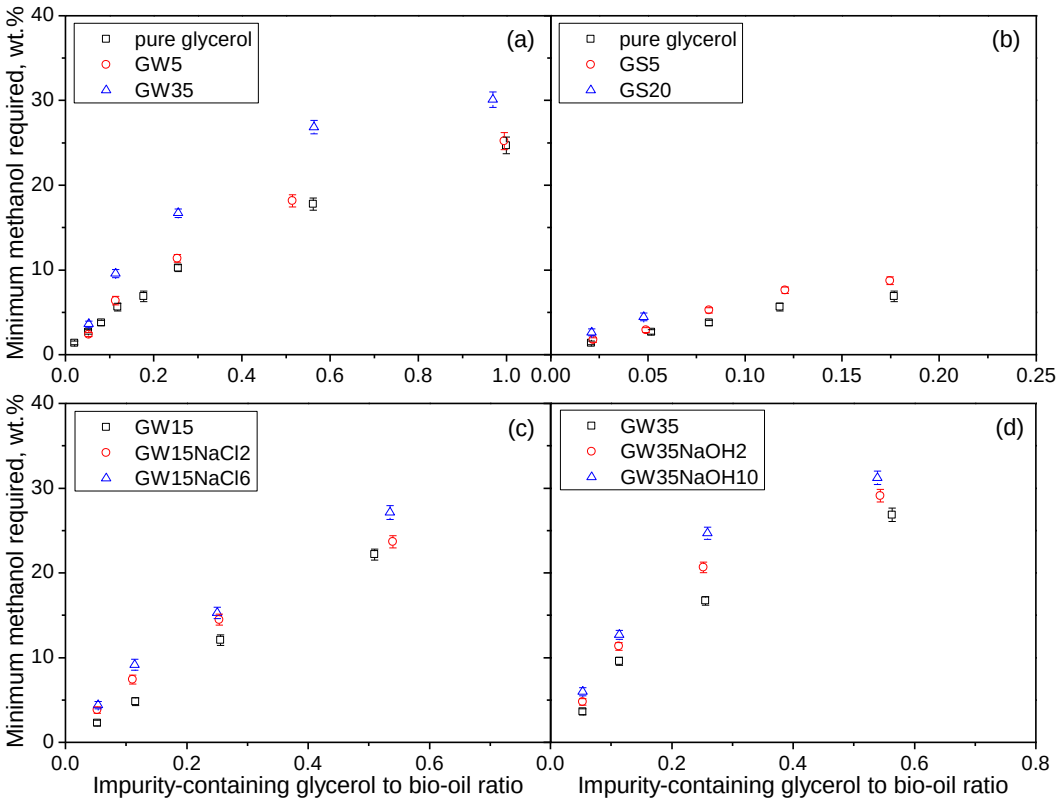

Figure 8-2 Solubility of impurity-containing glycerol in bio-oil: (a) water, (b) soap, (c) NaCl and (d) NaOH. GW5, GW15 and GW35: glycerol–water mixtures with water contents of 5, 15 and 35 wt% respectively; GS5 and GS20: glycerol–soap mixtures with soap contents of 5 and 20 wt% respectively; GW15NaCl2 and GW15NaCl6: aqueous glycerol solution GW15 with NaCl contents of 2 and 6 wt% respectively; GW35NaOH2 and GW35NaOH10: aqueous glycerol solution GW35 with NaOH contents of 2 and 10 wt% respectively

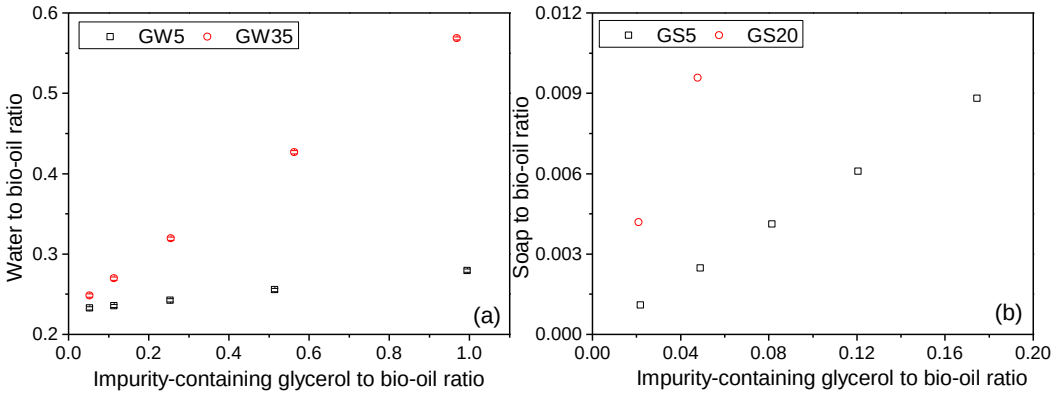

Figure 8-3 Water to bio-oil ratio (a) and soap to bio-oil ratio (b) based on weight of impurity-containing glycerol/bio-oil fuel mixtures as a function of impurity-containing glycerol to bio-oil ratio used for preparing the fuel the mixtures. GW5 and GW35: glycerol–water mixtures with water contents of 5 and 35 wt% respectively. GS5 and GS20: glycerol–soap mixtures with soap contents of 5 and 20 wt% respectively

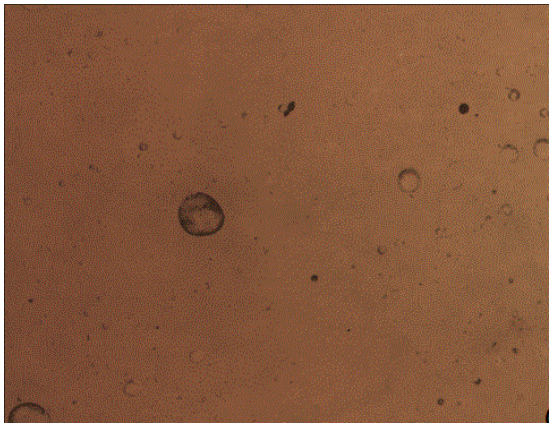

Figure 8-4 Microscope picture of a GS5/methanol/bio-oil blend with a soap to bio-oil mass ratio over 0.01. GS5: glycerol–soap mixture with soap content of 5 wt%

Third and last, panels c and d of Figure 8-2 show that the minimum percentage of methanol required for blending GW15NaCl and GW35NaOH mixtures into the

bio-oil is higher than that required for blending the corresponding GW mixtures into the bio-oil. This suggests that both NaCl and NaOH have adverse effect on the solubility of glycerol in the bio-oil. This is most likely due to the influence of these electrolyte matters on phase separation of the bio-oil. It is known that bio-oil has a complex colloidal system composed of hundreds of polar and non-polar compounds,[20,34] addition of ionic compounds may break down the weak equilibrium in the system and cause phase separation. Salt-induced phase separation of bio-oil has been reported and such separation was attributed to the increase in ionic strength of bio-oil system and the breakdown of the network structure in the micellar system of bio-oil.[298,299] Similarly, NaOH in aqueous solution can dissociate into cation and anion, which can attract water or other polar compounds in bio-oil because of ionic solvation[300] and thereby aggravating phase separation of bio-oil. Therefore, it is not surprising that NaOH worsens the solubility in a similar manner as salt.

8.4 Effect of Major Impurities in Crude Glycerol on the Fuel Properties of Glycerol/Methanol/Bio-oil Blends

To compare the effect of major impurities in crude glycerol on properties of glycerol/methanol/bio-oil blend, ten fuel blends were prepared with the percentages of the bio-oil and methanol being fixed at 88.4 wt% and 7.0 wt% respectively and glycerol containing different proportion of impurities accounting for the rest 4.6 wt% of the blends. This composition is selected in consideration of the homogeneity of all blends and the recommended methanol proportion in the mixture (less than 10 wt%) as discussed in Chapter 7. Fuel properties including viscosity, surface tension, density, HHV and elemental composition of the ten blends are listed in Table 8-4. It can be seen that the fuel properties, except viscosity, of all the blends are similar, with HHV being 19 ± 1MJ/kg, density being 1.16 ± 0.02g/cm^3, and surface tension being 32 ± 1 mN/m. In addition, as shown in Figure 8-5, the rheological properties of all the blends are similar and follow the behaviour of Newtonian fluids when the

shear rate is greater than 50 s^{-1}. This is consistent with our previous studies on rheological properties of bio-oils and also those of glycerol/methanol/bio-oil blends.[27] The differences in the viscosity of the fuel blends can be mainly attributed to the differences in the water contents of the fuel blends (see Figure 8-6b and e). Therefore, the results in Table 8-4 and Figure 8-5 suggest that these impurities have insignificant effects on the fuel properties and flow behaviour of the blends within the range of compositions considered in this study.

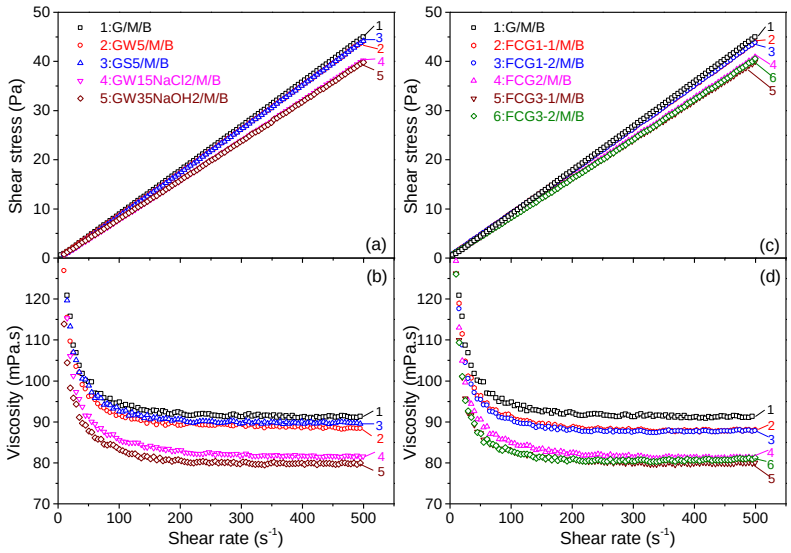

Figure 8-5 Shear stress and viscosity of selected fuel blends as a function of shear rate. G/M/B, GW5/M/B, GS5/M/B, GW15NaCl2/M/B, GW35NaOH2/M/B, FCG1-1/M/B, FCG1-2/M/B, FCG2/M/B, FCG3-1/M/B and FCG3-2/M/B: fuel blends consist of 4.6 wt% glycerol (G), 7.0 wt% methanol (M), plus 88.4 wt% bio-oil (B), GW5, GS5, GW15NaCl2, GW35NaOH2, FCG1-1, FCG1-2, FCG2, FCG3-1 or FCG3-2, respectively. GW5: glycerol–water mixtures with water contents of 5 wt%; GS5: glycerol–soap mixtures with soap contents of 5 wt%; GW15NaCl2: aqueous glycerol solution GW15 with NaCl contents of 2 wt%; GW35NaOH2: aqueous glycerol solution GW35 with NaOH contents of 2 wt%; FCG: formulated crude glycerol

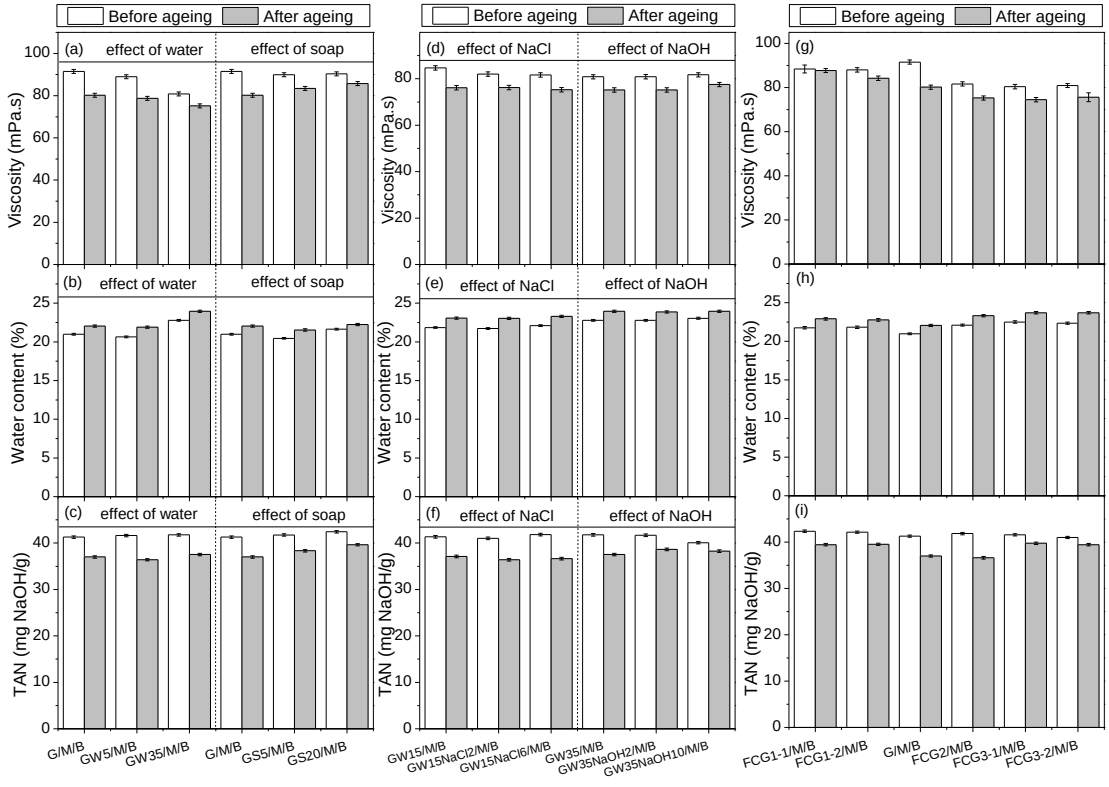

Figure 8-6 Changes in viscosity, water content and TAN of selected fuel blends before and after ageing. G/M/B, GW5/M/B, GW35/M/B, GS5/M/B, GS20/M/B, GW15NaCl2/M/B, GW15NaCl6/M/B, GW35NaOH2/M/B, GW35NaOH10/M/B, FCG1-1/M/B, FCG1-2/M/B, FCG2/M/B, FCG3-1/M/B and FCG3-2/M/B: fuel blends consist of 4.6 wt% glycerol (G), 7.0 wt% methanol (M), plus 88.4 wt% bio-oil (B), GW5, GW15, GW35,GS5, GS20, GW15NaCl2, GW15NaCl6, GW35NaOH2, GW35NaOH10, FCG1-1, FCG1-2, FCG2, FCG3-1 or FCG3-2, respectively; GW5, GW15 and GW35: glycerol–water mixtures with water contents of 5, 15 and 35 wt% respectively; GS5 and GS20: glycerol–soap mixtures with soap contents of 5 and 20 wt% respectively; GW15NaCl2 and GW15NaCl6: aqueous glycerol solution GW15 with NaCl contents of 2 and 6 wt% respectively; GW35NaOH2 and GW35NaOH10: aqueous glycerol solution GW35 with NaOH contents of 2 and 10 wt% respectively; FCG: formulated crude glycerol

Ageing experiments were conducted to investigate the long term stability of the glycerol/methanol/bio-oil blends in presence of the impurities. Viscosity, water content and TAN of the impurity-containing glycerol/methanol/bio-oil blends before and after ageing were evaluated and the results are shown in Figure 8-6. Decrease of viscosity and TAN and increase of water content were observed for all the blends. Such changes in these properties of the impurity-containing glycerol/methanol/bio-oil blends are consistent with those of the glycerol/methanol/bio-oil blends in our previous study [301]. The decrease of viscosity is associated with the increase of water content, and esterification between acids in bio-oil and glycerol or methanol was reported to be the primary reaction occurred in the mixture responsible for the changes of water content and TAN [301]. It is noted that the water content of the GW/methanol/bio-oil blends was increased from ~20.6% to ~22.8% (see Figure 8-6b) when the water percentage in GW increased from 5% to 35%, however the changes in water content or TAN (see Figure 8-6c) of these blends before and after ageing are similar to that of the glycerol/methanol/bio-oil blend (i.e. ~1.1% and ~10% for water content and TAN change respectively). This implies that the presence of water in glycerol has little effect on the reactions which may take place in the blends during ageing. Likewise, the changes in viscosity, water content and TAN were also not affected by the presence of NaCl as seen in Figure 8-6(d–f). However, for alkaline impurities in glycerol, the change in TAN was slightly reduced, especially when the crude glycerol containing high contents of impurities (e.g., 10% of NaOH or 20% of soap). This may be due to that the acid–base reactions between acidic compounds in bio-oil and the added NaOH result in lower TAN of the fuel blends, taking place even before ageing. It is also noted that the TAN of the GW35NaOH10/methanol/bio-oil blend is nearly the same as that of the GW35/bio-oil/methanol blend after ageing, suggesting that the availability of reactive acids in the bio-oil appears to be the limiting factor for further TAN decline in the GW35NaOH/methanol/bio-oil system. This is different to the

GS/methanol/bio-oil blends, for which after ageing, the TAN is slightly higher than that of the glycerol/methanol/bio-oil blend. This may be due to that the reactions between soap and acids in bio-oil lead to weaker acids that cannot participate in the esterification reactions during ageing of bio-oil. Overall, the contents of the impurities in the composed blends are generally low and these impurities have limited effect on the trends in changing viscosity, water content and TAN of the glycerol/methanol/bio-oil blends during ageing.

Table 8-4 Fuel properties of selected fuel blends

Blends	Elemental analysis (wt%)[a]				Heating value	Viscosity	Surface tension	Density
	C	H	N	O[b]	HHV (MJ/kg)[a]	(mP.s, @25 ℃)	(mN/m,@25 ℃)	(g/cm^3,@25 ℃)
G/M/B	42.12	7.95	0.19	49.75	19.00	91.5	32.95	1.14
GW5/M/B	42.03	7.95	0.19	49.83	18.97	89.0	32.28	1.12
GW15/M/B	41.85	7.96	0.19	50.00	18.93	72.4	32.30	1.16
GW35/M/B	41.48	7.98	0.19	50.34	18.84	69.6	32.58	1.17
GS5/M/B	42.18	7.95	0.19	49.67	19.02	83.5	32.32	1.16
GS20/M/B	42.39	7.97	0.19	49.45	19.09	83.9	31.36	1.17
GW35NaOH2/M/B	41.46	7.98	0.19	50.32	18.83	72.6	32.61	1.15
GW35NaOH10/M/B	41.81	7.97	0.19	50.14	18.93	81.7	32.84	1.17
GW15NaCl2/M/B	41.38	7.94	0.19	50.03	18.77	67.7	32.65	1.16
GW15NaCl6/M/B (FCG2/M/B)	41.76	7.94	0.19	49.84	18.88	79.2	31.65	1.17
FCG1-1/M/B	42.23	7.96	0.19	49.56	19.04	88.4	30.98	1.16
FCG1-2/M/B	42.13	7.95	0.19	49.67	19.00	88.0	30.96	1.18
FCG3-1/M/B	41.87	7.97	0.19	49.83	18.94	80.5	31.13	1.16
FCG3-2/M/B	41.69	7.98	0.19	49.99	18.89	80.9	31.07	1.16

[a] calculated value; [b] by difference. G/M/B, GW5/M/B, GW35/M/B, GS5/M/B, GS20/M/B, GW15NaCl2/M/B, GW15NaCl6/M/B, GW35NaOH2/M/B, GW35NaOH10/M/B, FCG1-1/M/B, FCG1-2/M/B, FCG2/M/B, FCG3-1/M/B and FCG3-2/M/B: fuel blends consist of 7.0% methanol (M), 88.4% bio-oil (B), plus 4.6% glycerol (G), GW5, GW15, GW35,GS5, GS20, GW15NaCl2, GW15NaCl6, GW35NaOH2, GW35NaOH10, FCG1-1, FCG1-2, FCG2, FCG3-1 or FCG3-2, respectively. GW5, GW15 and GW35: glycerol–water mixtures with water contents of 5, 15 and 35% respectively; GS5 and GS20: glycerol–soap mixtures with soap contents of 5 and 20% respectively; GW15NaCl2 and GW15NaCl6: aqueous glycerol solution GW15 with NaCl contents of 2 and 6% respectively; GW35NaOH2 and GW35NaOH10: aqueous glycerol solution GW35 with NaOH contents of 2 and 10% respectively; FCG: formulated crude glycerol

8.5 Solubility and Fuel Properties of Formulated Crude-Glycerol/Methanol/Bio-oil System

As the composition of crude glycerol from different biodiesel production process varies significantly, investigations on formulated crude glycerol (FCG) in addition to individual impurities can provide further guidance for blending crude glycerol with bio-oil. Solubility of FCG in the bio-oil is also characterised by the minimum percentage of methanol required to obtain a homogeneous blend, and the results are shown in a ternary diagram in Figure 8-7. Considering that homogenous FCG/methanol/bio-oil blend could not be formed when the soap to bio-oil mass ratio is over 0.01 (corresponding to a max of 11 wt% of FCG in the bio-oil, as discussed in section 8.3), the ternary diagram is scaled to show the solubility range of 0–25% of FCG in the bio-oil. It can be seen in Figure 8-7 that both FCG3-1 and FCG3-2 require more methanol to be dissolved in the bio-oil compared to FCG1-1 and FCG1-2, especially when the fuel blends have high contents of FCGs (e.g., ≥5 wt%). Such a difference may be caused by the difference in the water contents of FCG1 and FCG3 (see Table 8-3). When comparing FCG1-1 with FCG1-2, it can be seen that FCG1-2 with a lower soap content can be blended with the bio-oil with a wider range of solubility. This is also consistent with the discussion on the effect of soap on solubility in section 8.3. The solubilities of pure glycerol and FCG2 (with same composition as GW15NaCl6) in the bio-oil are also compared in Figure 8-7. It can be seen that the minimum methanol percentage required for blending FCG2 into the bio-oil is similar to that required for blending FCG1-1 or FCG1-2, and the solubilities of all FCGs in the bio-oil become worse than that of pure glycerol due to the adverse effect of impurities.

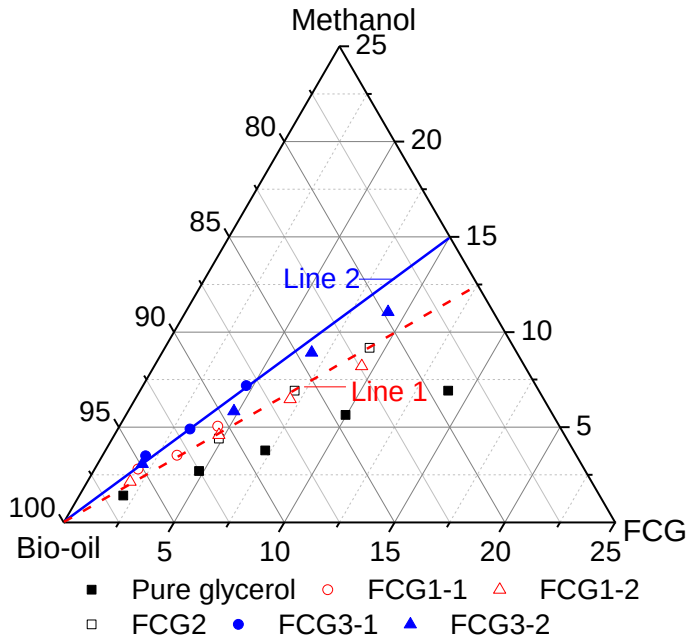

Figure 8-7 Solubility of formulated crude glycerol (FCG)/methanol/bio-oil system. Line 1 and Line 2 represent fuel blends with FCG to methanol mass ratio of 1:1 and 1:1.5 respectively

To evaluate the properties of the blends composed of bio-oil, methanol and FCG1-1/FCG1-2 or FCG3-1/FCG3-2, efforts were taken to prepare four homogenous blends with constant percentages of methanol and bio-oil (7.0 and 88.4 wt%, respectively). The key fuel properties, rheological properties and ageing properties of these four blends are shown in Table 8-4, Figure 8-5b and Figure 8-6(g-i), respectively. The results are also compared with properties of the glycerol/methanol/bio-oil blend and FCG2/methanol/bio-oil blend. Table 8-4 shows that there are no significant differences in the fuel properties of different FCG/methanol/bio-oil blends, with HHV, surface tension and density being ~19 MJ/kg, ~31 mN/m and ~1.16 g/cm^3, respectively. The viscosities of FCG1/methanol/bio-oil blends are slightly higher (~88 mPa.s) than those of the FCG3 or FCG2/methanol/bio-oil blends (~80 mPa.s) due to the slightly lower water contents (see Figure 8-6h). The rheological properties of the FCG/methanol/bio-oil

blends (see Figure 8-5b) indicate that these blends are also dominantly Newtonian fluids, similar to the glycerol/methanol/bio-oil blend. In comparison to the glycerol/methanol/bio-oil blend and FCG2/methanol/bio-oil blend, the changes in the TAN of FCG1 or FCG3/methanol/bio-oil blends before and after ageing are slightly reduced (see Figure 8-6i), most likely due to the presence of alkaline matter (soap and NaOH) as aforementioned in Section 8.4.

8.6 Further Discussion and Implications

The results presented so far show that it is feasible to use crude glycerol from biodiesel production process for producing crude-glycerol/bio-oil blends. Therefore, it is possible to integrate the crude-glycerol/bio-oil blending process into the existing biodiesel production process. There may be three important considerations.

The first consideration is the preliminary selection of production processes based on solubility. As shown in Figure 8-1, crude glycerol can be sourced from process PSMR, PSMR-N and MRPS. As discussed in section 8.5, FCG3-1/FCG3-2, which represents the crude glycerol generated from process MRPS, requires more methanol to be blended into the bio-oil compared to FCG1-1/FCG1-2 and FCG2 that represent the crude glycerol from the PSMR and PSMR-N processes, respectively. In practice, it may be favoured to retain the required amount of methanol in crude glycerol for fuel blending, via adjusting methanol recovery in the process. The more methanol is required for blending, the less methanol can be recovered. As shown in Figure 8-7, the mass ratios of FCG to methanol in homogenous blends is ~1:1.5 and ~1:1 for FCG3 and FCG1 (or FCG2), respectively. The methanol recovery allowed for blending the FCG with the bio-oil can then be calculated, considering the contents of glycerol in FCG (see Table 8-3) following a previous method.[301] For instance, for FCG3, the methanol recovery is limited to ~16% even when methanol to oil ratio in feedstock is 10:1; while for FCG1 and FCG2, methanol recovery may be up to 37%

if feedstock with such methanol to oil molar ratio (10:1) is used in the respective PSMR and PSMR-N processes. As recovery of unreacted methanol can save input costs for the biodiesel production process,[42] the PSMR and PSMR-N processes that allow a max methanol recovery of 37% seems to be more suitable than process MRPS that only allow a max methanol recovery of 16%. In addition, although the PSMR-N process is more complex than the PSMR process, the process complexity may be offset by better fuel blend quality so that there may be a trade-off between process complexity and fuel blend product quality.

The second consideration is the comparison in the properties of fuel blends composed of bio-oil and crude glycerol from the preliminarily selected processes. As discussed in Section 8.5, there is little difference in the fuel properties or rheological properties between FCG1/methanol/bio-oil blends and FCG2/methanol/bio-oil blends. The FCG1/methanol/bio-oil blends have better stability as there are only slightly reductions in the changes in the TANs during ageing, However, the acidity of these blends after ageing is higher than that of the FCG2/methanol/bio-oil blend due to presence of soap. In addition, the presence of alkaline matters in FCG1 (or salt in FCG2) introduces a high amount of inorganic species (Na for FCG1; Na and Cl for FCG2) in the fuel blends. As sodium is sourced from the catalyst used for biodiesel production, the sodium content in crude glycerol from the MRPS and the MRPS-N processes should be similar if the same feedstock is used. The anion introduced by salt (in this case, Cl) into the fuel blends can also cause various ash-related issues during gasification or combustion.[302,303] For this reason, blends of bio-oil and crude glycerol from the PSMR process may have better properties for combustion applications. Overall, Table 8-5 shows that the sodium contents in the FCG/methanol/bio-oil blends with same bio-oil and methanol proportion are in same order of magnitude, which are however one or two orders of magnitude smaller than that in FCG with methanol (1:1.5, by weight) or FCG. This in turn shows the advantage in blending crude glycerol into bio-oil as the fuel blends can effectively

dilute the high concentrations of inorganic species in crude glycerol hence minimize the potential ash-related issues during combustion/gasification.

Table 8-5 Sodium content (ppm) in formulated crude glycerol (FCG), FCG with 60 wt% methanol and blends with 4.6 wt% FCG, 7.0 wt% methanol and 88.4 wt% bio-oil

NO.	FCG	FCG with 60% methanol	FCG/methanol/bio-oil blend
1-1	23,096.7	9,234.7	1,077.9
1-2	17,643.0	7,030.3	823.7
2	23,328.0	9,338.6	1,085.0
3-1	40,334.2	16,063.6	1,876.6
3-2	34,869.0	13,942.6	1,628.4

The third and last consideration is feed configuration of the selected PSMR process for generating crude glycerol, including methanol to oil ratio, catalyst usage and FFA content in feed oil. Due to the presence of impurities, more methanol is required to enable the dissolution of crude glycerol than the pure glycerol into the bio-oil for fuel blend production. Therefore, the methanol to oil ratio in the feedstock of biodiesel production process is an important factor. For instance, for FCG1 to be blended into the bio-oil, the methanol to oil molar ratio should be no less than 7:1. Therefore, feed configuration with a relatively high methanol to oil molar ratio (7:1–10:1) may be preferable for producing crude glycerol suitable for blending with the bio-oil. As for catalyst usage, the requirement for the fuel blending process may be consistent with that for biodiesel production process, taking into consideration the possible trade-off effects of NaOH on solubility and improved acidity of the fuel blends. As soap not only can worsen the solubility range of glycerol in the bio-oil but also can hinder TAN decline during ageing of the fuel blends, it is desirable to deploy feed oil of low FFA contents for biodiesel production. Overall, considering crude glycerol solubility in the bio-oil, process complexity, and product quality, the PSMR process and feed with relatively high methanol to oil molar ratios (7:1–10:1) for biodiesel production are recommended for integrating the crude glycerol/bio-oil blending process into the

existing biodiesel production process, as illustrated in Figure 8-8. As the blending ratio of the crude glycerol and bio-oil can be affected by the contents of soap and methanol in crude glycerol, suitable crude glycerol/bio-oil blends from process PSMR may be produced if the content of the bio-oil is ≥88 wt% in the fuel blends while the contents of methanol and soap in the crude glycerol is ≥50 wt% and ≤ 20 wt%, respectively.

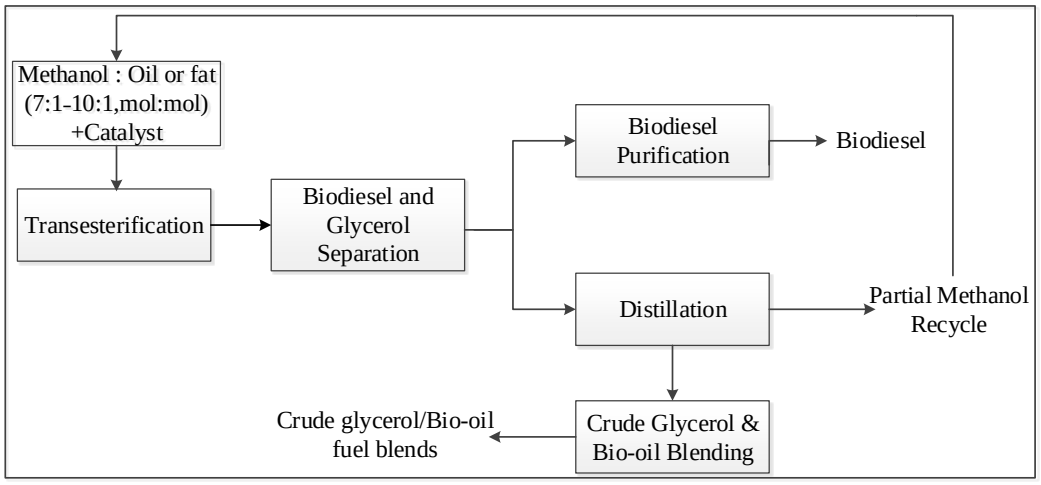

Figure 8-8 A proposed strategy for integrating the crude-glycerol/bio-oil blending process into the existing biodiesel production process

8.7 Conclusions

The major impurities in crude glycerol, water, soap, NaCl and NaOH, can have different adverse influence on the solubility of glycerol in the bio-oil. In general, NaCl and NaOH can worsen the solubility even at a low concentration of 2 wt% in glycerol because of their capability to aid phase separation of bio-oil. For water and soap, their effect on solubility becomes significant when the mass ratio of water to bio-oil or the mass ratio of soap to bio-oil is over 0.3 and 0.01 respectively. Although the impurity-containing glycerol/methanol/bio-oil blends with the composition studied show similar rheological properties and fuel properties (e.g., heating value, surface tension and density etc.) as to that of the glycerol/methanol/bio-oil blend,

slight reduction on acidity of fuel blends is observed upon presence of high content (e.g., 10 wt%) of NaOH in aqueous glycerol mixture. The ageing of glycerol/methanol/bio-oil blend is also influenced by the impurities. Particularly, the presence of alkaline matter (soap or NaOH) leads to less changes in the fuel properties (viscosity, water content and acidity) during long term storage. In addition, solubility of formulated crude glycerol (FCG) in the bio-oil and properties of the FCG/methanol/bio-oil blends were studied. The results suggest that it is favourable to integrate the blending process of crude glycerol and the bio-oil into the biodiesel production process without water addition to aid phase separation and neutralisation of glycerol phase.

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CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Introduction

This chapter summarizes the key findings from the present study. Overall, the thesis has obtained essential knowledge on properties of two bio-oil-based fuel mixtures, i.e. biochar/bio-oil slurry fuel (bioslurry) and glycerol/bio-oil fuel blends. Firstly, a new quantification method was established for analysing alkali and alkaline earth metallic (AAEM) species in bio-oil and bioslurry fuels. Secondly, this research has investigated into evolution of fuel properties and ageing during bioslurry storage. Thirdly, fundamental understanding on leaching characteristic of biochar by bio-oil model compounds was achieved in this study, which is of great importance for mitigating undesired distribution of AAEM species in a bioslurry system. Fourthly, this research has reported as the first time in the field on phase behaviour and fuel properties of glycerol/methanol/bio-oil fuel blends. Finally, it has been demonstrated in this study about the effect of major impurities in crude glycerol on the solubility and properties of glycerol/methanol/bio-oil fuel blends, and then a possible strategy was proposed for utilization of crude glycerol from biodiesel industry. In addition, this chapter also provides some recommendations on future work in this area based on the conclusions and evaluations of the present research.

9.2 Conclusions

9.2.1 A Method for the Quantification of Alkali and Alkaline Earth Metallic Species in Bioslurry Fuels

- Conventional ashing–digestion–IC method that is designed for quantifying AAEM species in solid fuels underestimates these values in bioslurry fuels due to carry-over of biochar particles during ashing;

- The evaporation step consists of multi-steps of slow heating and holding at various segment temperatures corresponding to the boiling points of the major compounds in bio-oil, resulting in progressive evaporation of bio-oil vapours with little carry-over of biochar particles;
- The new evaporation–ashing–digestion–IC method can accurately determine the concentrations of AAEM species in bio-oil or bioslurry fuels, with the relative standard errors being within ±3% and the limitations of quantification being 0.4−3.0 ppm.

9.2.2 Fuel Properties Evolution and Aging during Bioslurry Storage

- Biochar has significant influence on the changes in fuel properties of the bio-oil phase in bioslurry. While the blank bio-oil samples showed negligible change, the presence of biochar in the bioslurry fuels leads to significant changes in fuel properties during 29 days storage;
- The reduction of TAN and viscosity, and the increase of water content were observed in the bio-oil, at least partially due to some condensation reactions among bio-oil compounds catalysed by the biochar or reactions between the acidic bio-oil and the basic biochar;
- An increase in biochar loading level leads to further reduction in the TAN and viscosity, and increase in the water content in the bio-oil phase during bioslurry storage;
- Bislurry storage also leads to undesired redistribution of AAEM species between the biochar and bio-oil phase. The leaching of these inorganic species into the acidic bio-oil phase follows two-step kinetics.

9.2.3 Leaching Characteristics of Alkali and Alkaline Earth Metallic Species from Biochar by Bio-oil Model Compounds

- Leaching of AAEM species from biochar by bio-oil is mostly attributed to the

water soluble fraction of bio-oil, especially the organic acids and water in bio-oil;

- The leaching capability of other individual organic compound (such as methanol, acetone and guaiacol) in bio-oil appears to be limited due to poor polarity or low dielectric constant;
- The presence of these organic compounds can have significant impact on the leaching capability of water or acids;
- Leaching of AAEM species by water can be hindered in presence of organic compounds with lower polarity or dielectric constant due to the decrease of salt solubility;
- The presence of phenolic compounds may enhance the leaching of the AAEM species (especially Ca and Mg), likely due to the ability to penetrate into biochar structure and thus increase the accessibility of AAEM species by water or acids.

9.2.4 Phase Behaviour and Fuel Properties of Glycerol/Methanol/Bio-Oil Blends

- Although the solubility of glycerol in the bio-oil is poor, homogenous ternary glycerol/methanol/bio-oil blends can be obtained, with the aid of proper amount of methanol;
- The fuel properties of such blends including heating value, viscosity, surface tension etc. are improved compared to the bio-oil or glycerol as an individual fuel;
- Considering safe storage and handling of a fuel and the possible glycerol to methanol ratio that might be obtained from biodiesel production system, blends with a composition range (bio-oil ≥ 70 wt%; glycerol ≤ 20 wt%; methanol ≤ 10 wt%) are recommended as potential burner fuels;
- The accelerated aging tests of the fuel blends show that the properties of the fuel blends can change upon long term storage, i.e. noticeably decreases in viscosity and TAN accompanied with an increase in the water content.

9.2.5 Effect of Major Impurities in Crude Glycerol on Solubility and Properties of Glycerol/Methanol/Bio-oil Blends

- The major impurities in crude glycerol (water, soap, NaCl and NaOH) can have different adverse influence on the solubility of glycerol in the bio-oil;
- The effect of water and soap on glycerol solubility in bio-oil only becomes significant when the water to bio-oil ratio or the soap to bio-oil ratio exceeds 0.3 and 0.01(by weight), respectively;
- Salt (NaCl) and alkaline catalyst (NaOH) can severely worsen the solubility of glycerol in the bio-oil even at a concentration of 2 wt% in the glycerol aqueous solutions;
- Compared to solubility, the rheological properties and fuel properties (including heating value, surface tension and density etc.) of the glycerol/methanol/bio-oil blends are little influenced by these impurities, except the acidity being slightly reduced for fuel blends containing high content of NaOH (e.g.,10 wt% of NaOH in aqueous glycerol solution);
- Ageing of the glycerol/methanol/bio-oil blend is influenced by the impurities. Particularly, the presence of alkaline matter (soap or NaOH) leads to less changes in the fuel properties (viscosity, water content and acidity) during long term storage;
- Further investigations on solubility of formulated crude glycerol (FCG) in bio-oil and properties of the FCG/methanol/bio-oil blends suggest that the crude-glycerol/bio-oil blends production process can be potentially integrated into the biodiesel production process without water addition to aid phase separation and neutralisation of glycerol phase.

9.3 Recommendations

On the basis of the outcome of this PhD project, recommendations for future

research are suggested in consideration of several new research gaps identified:

1. Organic solvents like methanol or acetone can inhibit water leaching of AAEM species from biochar, thereby being considered capable of controlling the unwanted redistribution in a bioslurry system (Chapter 6). Further research is needed to investigate the distribution of AAEM species in a bioslurry system with addition of these solvents, and how the existing form of inherent AAEM species affects the property change of bioslurry;
2. Chapter 7 and 8 have studied fuel properties of glycerol/bio-oil blends (with methanol and/or other impurities in crude glycerol), including viscosity, water content, surface tension, density, and HHV etc. Future work is needed to characterise additional fuel properties of such blends including pour point, cloud point and freezing point, in consideration of the high freezing point of glycerol.[167] Therefore, systematic studies should be carried out to study the cold flow behaviour of the obtained (crude) glycerol/bio-oil blends;
3. In this study, the whole bio-oil was used to blend with glycerol. Considering the polarity similarity, glycerol may have better solubility in the bio-oil water soluble fraction compared to in the whole bio-oil. Therefore, a co-production strategy may be considered to use bio-oil water soluble fraction to produce fuel blends with glycerol, and use the bio-oil water insoluble fraction as feedstock for phenol replacement production;
4. Fuel quality of bio-oil-based fuel mixtures (bioslurry fuels and fuel blends with glycerol) seems to be suitable for combustion application. However, combustion behaviour or atomization characteristics of these fuel mixtures should be investigated to collect data for practical application.

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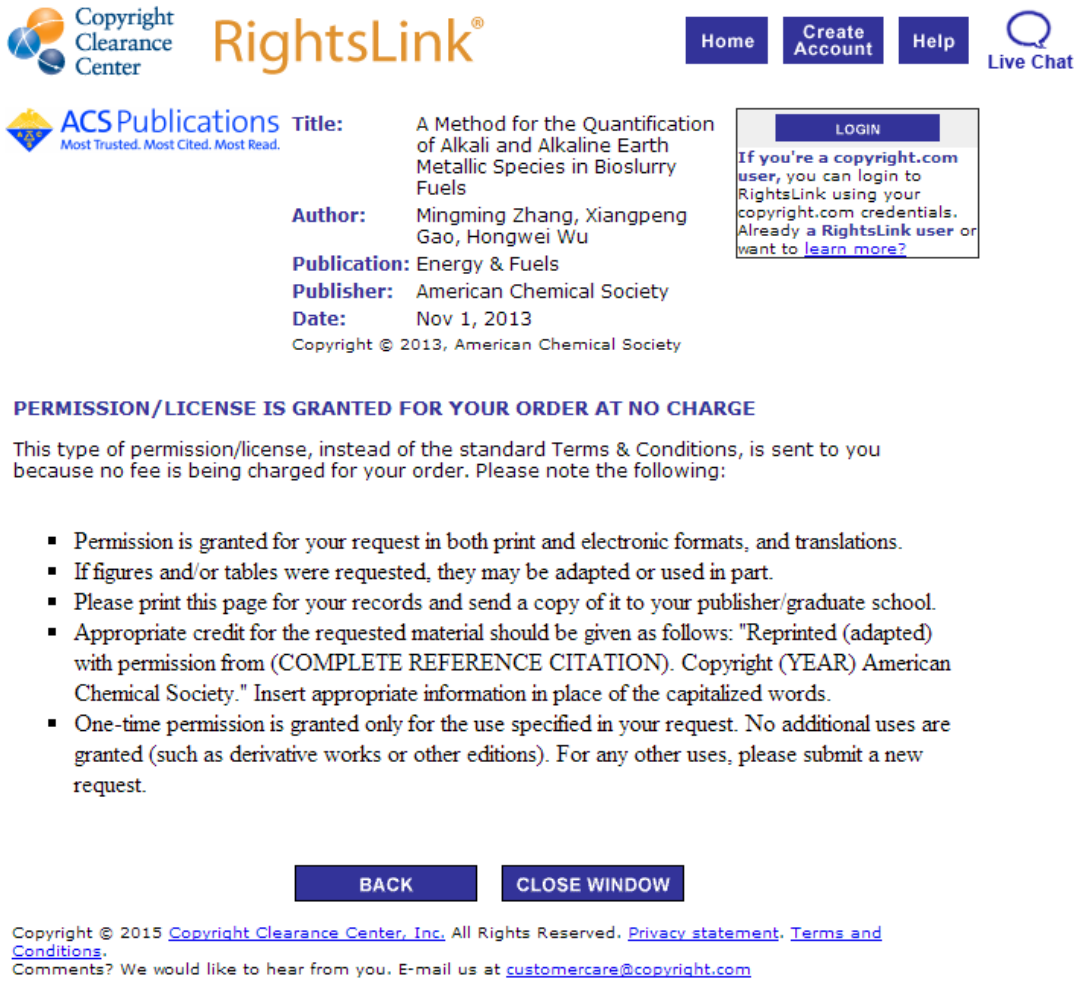

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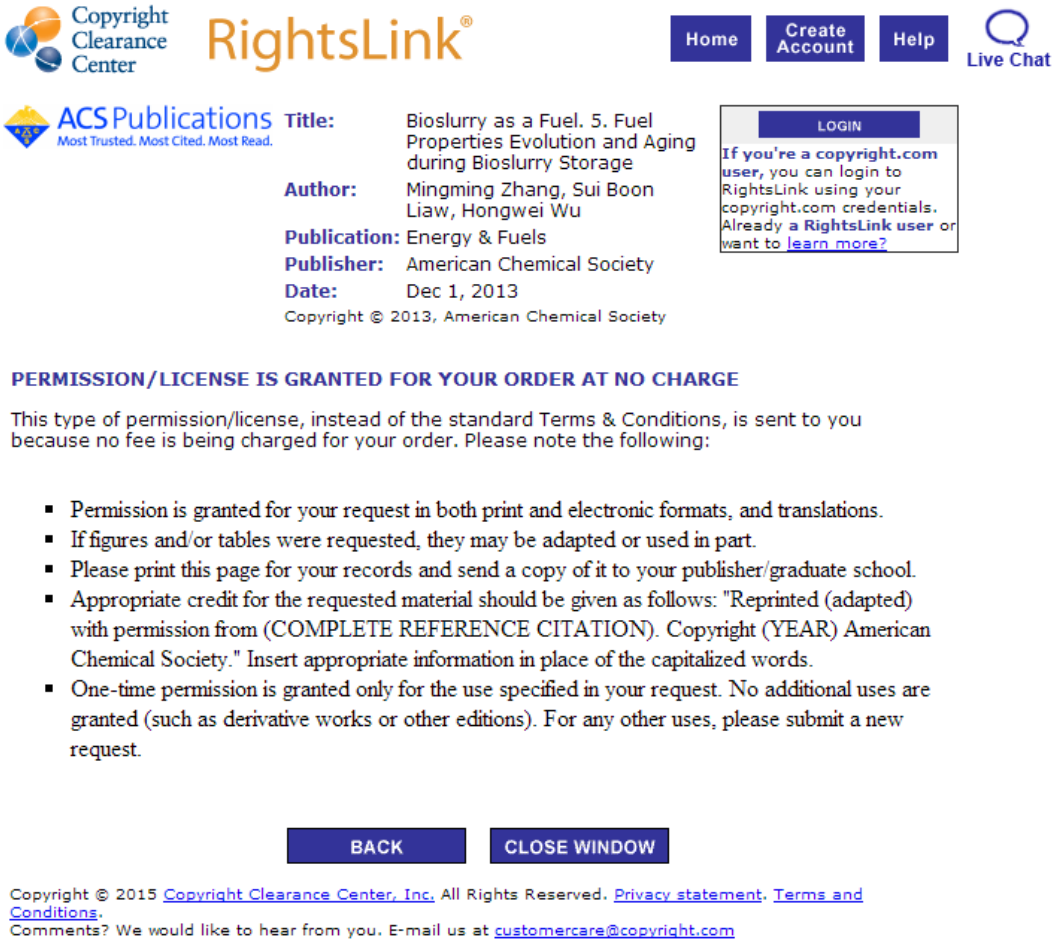

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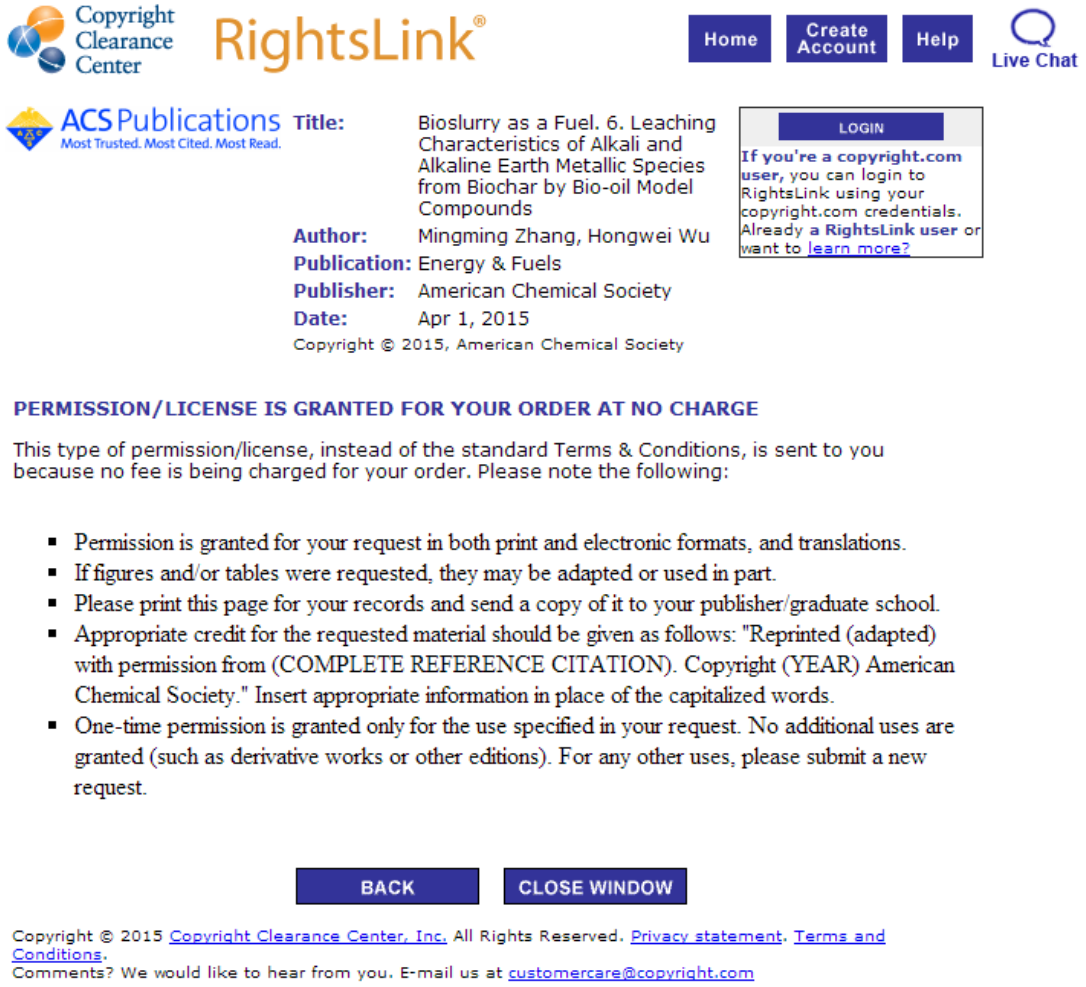

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Author: Mingming Zhang, Hongwei Wu

Publication: Energy & Fuels

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Date: Apr 1, 2015

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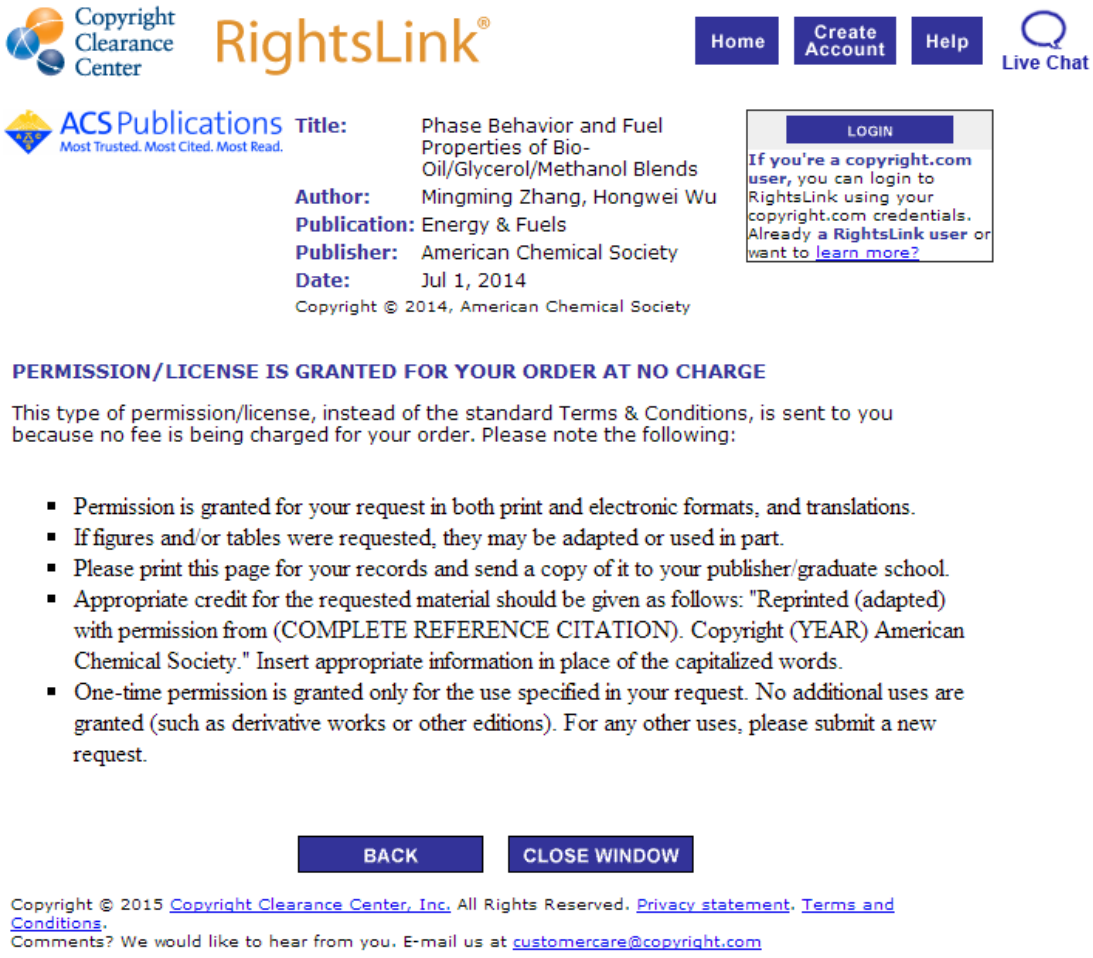

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